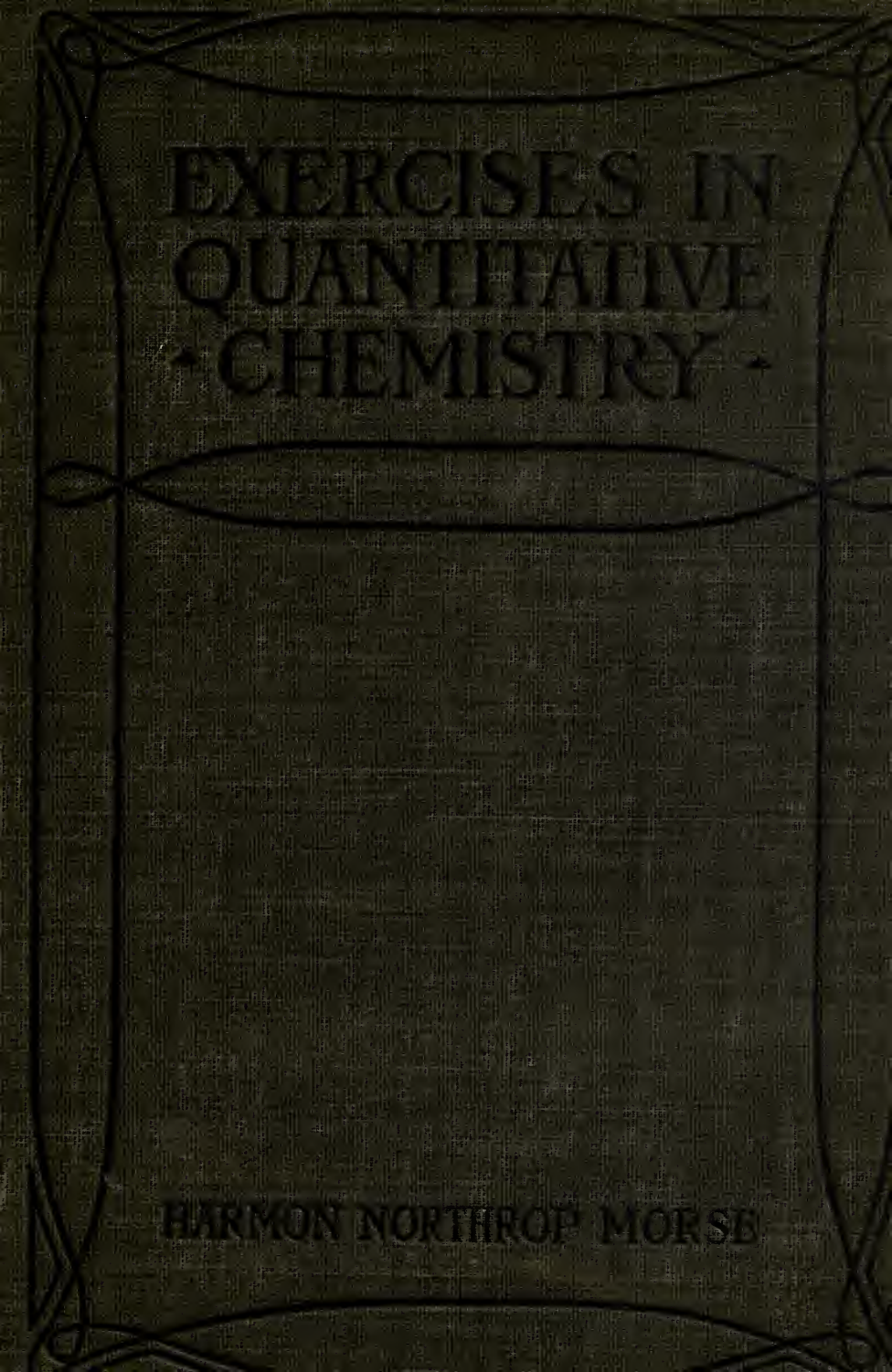




EXERCISES IN QUANTITATIVE CHEMISTRY

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EXERCISES IN QUANTITATIVE CHEMISTRY

BY

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PREFACE

The essential portions of this book have been in use in the author's laboratory for several years in the form of mimeographed notes, which were revised and expanded from time to time until they became too voluminous for further duplication by this process. Hence they have been put in book form for the use of the author's students and of any others who may find them of service.

The purpose which the author had in view in preparing the notes was twofold. First, to economize the energy of the student by placing in his hands a working guide sufficiently precise to keep him in the right path during the absence of his teacher, and secondly, to increase the efficiency of the teacher by saving him waste of time and effort in repairing the grosser mistakes of inexperienced students.

The book is not intended as a *complete* guide, even in the matters contained therein. Enough — and probably more than he can do to his satisfaction — has been left for the teacher, from whom the student may justly expect at all times the warning, suggestion, or amplification which will contribute most effectively to his progress and discipline.

The problem of a wise choice of exercises for the student of quantitative chemistry is a difficult one. It is much more complex than formerly, when the greater portion of the student's time in the laboratory was devoted, as a matter of course, to analytical chemistry. It was possible then to train expert analysts. At the present time this is not practicable, except at the expense of other work which is everywhere regarded as indispensable. The chemical student in training for his calling

is now required to take somewhat protracted courses of experimental work, which are arranged with a view to familiarizing him with the important reactions of substances, and that without any reference to the utility of such work for the purposes of analytical chemistry. To this end, he is expected to prepare a great number of typical compounds, both organic and inorganic. He is also required to exercise himself in the methods peculiar to physical chemistry. Hence the time which can be devoted to his training in quantitative chemistry is shorter than formerly, and the problem of what to give him to do in this field is a perplexing one. To the author it has seemed best to select the limited amount of work which the student can do with a view to giving him a familiarity with the greatest practicable variety of quantitative methods and operations, and not to endeavor to train him especially as an analyst. This book is, therefore, not an *analytical chemistry*. It is believed, however, that a student who, under competent guidance, has done well the work which is here prescribed will have acquired a skill in quantitative manipulation and a knowledge of methods which will enable him quickly and easily, with the aid of the many existing excellent works of reference, to become proficient in any of the several lines of quantitative analytical chemistry; and this, it appears to the author, is the end to be sought, and the best that can be hoped for under the present conditions.

In the last two chapters of the book an account is given of certain new electrical heating appliances for laboratory use, which the author has found quite serviceable; also of a new electrical method for the combustion of organic compounds, which in his laboratory has almost entirely supplanted the older process.

HARMON N. MORSE

MAY 1, 1905

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QUANTITATIVE EXERCISES

CHAPTER I

THE BALANCE

The object to be accomplished by weighing is to determine the amount of matter in materials, i.e. their *mass*; and the *weights* which are used in the process are to be regarded merely as standard *masses*. In weighing, that is in comparing objects with the weights with respect to their mass, the force of gravity is utilized. This force varies with latitude and with elevation above sea level; but the results of weighing are not altered by change of locality, since the object and the standard with which it is compared are affected in the same degree by the change. It is only in the weighing of gases, when the relation of weight to volume is to be determined, that the fact of the variable intensity of the earth's attraction must be taken into consideration by the chemist.

The balance used by chemists in determining weight is a lever whose two arms are of equal length and weight. This lever is known as the *beam*, and the form which is given to it is that which is supposed to combine a maximum of rigidity with a minimum of weight. The material of which it is made is usually brass, though sometimes an alloy of aluminium with other metals is used.

The axis about which the beam rotates is the sharp edge of a wedge-shaped piece of agate or of hardened steel. This is known as the *central knife edge*. It is placed at right angles to the vertical plane in which the beam is to move, and a little above the center of gravity. Hence the beam can move in but

one plane, and it always tends, when left alone, to take a horizontal position. The central knife edge rests upon a plate of agate which is fixed in a horizontal position at the top of the *standard*.

The loads — the object to be weighed and the weights — are suspended from the two ends of the beam at equal distances from the axis of rotation. The arrangement for the suspension of each of the two loads consists of three parts: (1) a *terminal knife edge* of agate or steel which is fastened to the beam with its sharp edge parallel to the central knife edge and pointing upwards; (2) a *stirrup* holding an agate plate which is hung upon the knife edge; and (3) a *pan* which is suspended from the stirrup (usually) by means of a jointed hook. Two things are essential with respect to the position of the loads: (1) the points from which they are suspended must always maintain, during any given experiment, the same relative distance from the axis; (2) the point of suspension and the center of gravity of a load must fall in the same vertical line whatever the position of the beam. The first condition is fulfilled by placing the terminal knife edges parallel to the central one; and the second, by giving the pan freedom of rotation in two planes, one of which is the plane in which the beam moves, and the other a plane at right angles to it, i.e. about the terminal knife edge and on the jointed hook. A second knife edge placed in the stirrup at right angles to the terminal one upon the beam is sometimes substituted for the joint in the hook. Again, in some balances the pan is suspended from the stirrup by means of a chain of several links.

If the knife edges are allowed to remain continuously in contact with their bearings, the former soon become dull, and furrows are worn into the latter, rendering the balance incapable of accurate weighing. Every instrument is therefore provided with a device called the *arrest*, which raises the beam and at the same time lifts the stirrups and pans, thus separating all three of the knife edges from their bearings.

Owing to corrosion, accumulation of dust, or unequal expansion of the arms, one side of the balance (arm, stirrup, and pan) sometimes becomes heavier or acquires a greater leverage than the other, so that the beam does not assume a horizontal position in a state of rest. To remedy this difficulty balances are provided with an arrangement by which the leverage of one of the arms may be increased or diminished. This consists sometimes of a movable vane placed above the center of the beam, and sometimes of a nut running upon a screw which is attached to one end of the beam.

To determine when the beam is in a horizontal position and also to enable one to judge its movements with precision, a long pointer is attached to it in front of the central knife edge. The pointer makes right angles with the plane of the three knife edges, and its lower end vibrates, when the beam is in motion, before or just above a graduated ivory scale which is situated at the base of the standard.

An essential feature of every balance is the device by which the distance between the center of gravity of the beam and the axis of its rotation is regulated. This consists sometimes of an adjustable bob upon the pointer, and sometimes of a screw and nut placed vertically above the center of the beam.

Finally, every balance is provided with a spirit level or a plumb line to determine when the plane of the knife edges is horizontal, and with a case to protect it from dust, sudden changes of temperature, and draughts of air.

A balance must be accurate and sufficiently sensitive to meet the requirements of the work to be done with it. The following are the more important of the conditions which affect these qualities.

The Position of the Center of Gravity. In order that the beam may always tend to take a horizontal position, the center of gravity of the balance (beam, stirrups, and pan) together with

the loads upon the pans must lie below the axis of rotation. If the center of gravity were in the axis, the equilibrium would be indifferent and the beam would remain in any position which might be given to it. If it were above the axis, the equilibrium would be unstable and the beam once moved from its horizontal position could not return to it.

The Distance between the Center of Gravity and the Axis. The *sensibility* of the balance (which is the angle through which the beam will turn for a given difference of load upon the two pans, and which, therefore, determines the precision with which objects may be weighed) depends mainly upon the distance between the center of gravity and the axis of the beam's rotation. The shorter the distance between them the more sensitive is the balance. Hence the utility of the provision which is made in the construction of every fine balance for the raising or lowering of the center of gravity according to the fineness of the work which is required of it. Of the two arrangements for this purpose already referred to in the description of the balance, namely the threaded post and nut placed above the center of the beam and the movable bob attached to the pointer by means of a set-screw, the former is much more easily managed, and is therefore to be preferred.

As the distance between the center of gravity and the axis is diminished by raising the former, the beam vibrates more slowly. The sensibility of any given balance may therefore be judged by the *time of vibration* of the beam, or, what is the same thing, by the time consumed by the end of the pointer in making two successive excursions past any fixed point of the scale at the foot of the standard.

The Knife Edges must be Parallel. The evil consequences of the lack of parallelism are numerous, and they vary according to the character of the defect. It will suffice to mention a single possible result, namely an unequal and varying distribution of the burdens along the knife edges, the effect of which would be a changeable ratio of the arm lengths.

The Three Knife Edges must lie in the Same Plane. This is a consequence of the fact that the loading of the pans (which is in effect the same as the loading of the terminal knife edges) changes the distance between the center of gravity and the axis, and thereby affects the sensibility of the balance. If the terminal knife edges are below the central one, the loading of the pans lowers the center of gravity and diminishes the sensibility. If they are in the same plane with it, or above it, the opposite effect is produced, and the loading of the pans increases the sensibility. But in the former case, i.e. when the three knife edges are in the same plane, the center of gravity can never reach the axis; hence the equilibrium can never become indifferent or unstable. In the construction of balances, however, it is permissible to elevate the plane of the terminal knife edges very slightly above the central one. When this is done, it is for the purpose of compensating for a loss of sensibility due to bending of the beam and to friction upon the knife edges.

The bending of the beam diminishes the sensibility by lowering the terminal knife edges; and, since no beam is perfectly rigid, the effect of bending upon the sensibility is usually noticed when a balance is heavily loaded. It will be seen that the extent to which the balance maker may elevate the terminal knife edges above the central one is limited by the condition that the center of gravity must not rise quite to the axis when the instrument is loaded to its maximum capacity.

The Length and Weight of the Beam. The sensibility of the balance depends also upon the length and weight of the beam. The longer the beam the greater the sensibility. The lighter the beam the greater the sensibility. Hence the rivalry between the long and the short beam balances. The former have the advantage of greater length of arm and the latter that of lighter weight. The short beam vibrates more quickly than the long one, and this fact is often cited as its principal advantage, the assumption being that quick vibration saves time in weighing. The benefit to be derived from this property of the

short beam is, perhaps, overestimated, for in careful weighing by correct methods rapid vibration is a positive disadvantage.

The Effect of Friction. Friction upon the knife edges diminishes the sensibility of the balance by increasing the difficulty with which the beam and the pans turn upon their axes. Any undue friction upon the terminal knife edges may also prevent the loads from acting downward in vertical lines, and thus, in effect, change the relative lengths of the arms. Great pains is taken in the construction of balances to reduce the friction to a minimum, and any considerable development of it in an instrument should be investigated at once. It may be due to dust between the knife edges and their bearings, to the rusting of the knife edges if they are made of steel, or to the dullness of the knife edges and the furrowed condition of the bearings. The last conditions develop in balances which are carelessly used or left to swing when not in use, and also in those which are subjected to constant jarring.

Equality of Arm Lengths. Equality in the length of the two arms is desirable but not essential, since for most purposes it is only necessary that the weights to be determined shall be relatively correct. If it is desired to obtain correct weighings, methods are employed which eliminate the errors arising from the inequality of the arms.

The Location of a Balance. A balance should be so located that the two arms will maintain, as nearly as possible, the same temperature and consequently the same relative length. Hence it should not be placed near a window, a door which is frequently opened, or an aperture through which hot or cold air enters the room. Other things being equal, it should be placed in the center of a room rather than at the side. If the light is sufficient, it is well to protect the balance from air currents by surrounding it on three or all sides by curtains of white material. A balance which is unfavorably situated as regards sources of heat or cold will manifest the fact by constantly changing its zero point, i.e. the position which the

pointer would take before the scale if the beam should come to rest after having been set in motion. If artificial light is used in weighing, the lamp or burner should be placed above and back of the head of the observer, and so located with respect to the beam that the heat from it will affect both arms equally. Whether the light is properly placed or not can be ascertained by taking several zero points in succession, — that is, by releasing the beam and pans at short intervals and determining by observing its excursions before the scale where the pointer will rest when the beam ceases to vibrate. If the arms are unequally heated by the lamp, the zero points will vary, tending constantly toward the side of the arm which is less rapidly warmed.

The foundation on which the balance rests should be as firm as possible. The constant jarring of a balance interferes with weighing by rendering the correct determination of zero points difficult or impossible, and it may seriously injure the knife edges and their bearings. The extent to which a balance is affected by the unsteadiness of its foundation may be ascertained by placing a thin glass bottle partly filled with mercury within the case and observing the movements on the surface of the metal. It is well, if practicable, to place the balance on a solid pier of masonry which extends some distance into the earth, and whose vertical sides do not come into contact either with the earth or with any of the floors of the building. A heavy wall is much more steady than a light one; hence a wall of brick or stone is to be preferred as a support to one of wood. A balance shelf may be attached to such walls by means of heavy iron brackets, but in no case should the shelf be partially supported by legs resting upon the floor. The effect of jarring upon a table resting on the floor may be considerably diminished by placing heavy weights upon it. An arrangement which is said to be effective for localities where it is otherwise impossible to secure a sufficiently steady foundation for balances is that which was first used in the provisional office of the K. K. Normal-Aichungs Commission of Austria. An air-tight box

capable of supporting a balance in a bath of glycerin is suspended in a frame by diverging chains attached to its four corners. Underneath this is placed a tank of glycerin. The balance is so located upon the box as to equalize the strain upon the chains, and glycerin is poured into the tank until the box with its burden is on the point of floating. There is also an arresting device operated by a wheel by means of which the box and balance on it may be raised and made steady during the introduction and removal of weights, etc.

Some basic substance, such as lime or an alkaline carbonate, should be kept in the balance case to neutralize acid vapors. It is also customary to place in the case some drying agent, like calcium chloride. The practice is, however, of doubtful utility except when the room in which the balance is kept is one of unusual humidity. Strong sulphuric acid should not be used as the drying agent, since the dust which falls into it may reduce the acid with formation of volatile products which are injurious to the balance.

PRECAUTIONS TO BE OBSERVED IN WEIGHING

1. Sit directly in front of the center of the balance so as to avoid parallax while observing the movements of the pointer.

2. See that the balance is level.

3. Release and arrest the beam and pans with a slow and steady movement of the hand. Jerky movements are sure to injure the knife edges. If practicable, the beam should be arrested only when it is in a horizontal position. The pads, or brushes, under the pans, which are designed to steady them while their loads are being placed in position or removed, should be lowered before releasing and raised again after arresting the beam and pans.

4. Avoid giving to the pans any rotary motion in a horizontal direction, and all other movements which would cause a knife edge to scrape on its bearing.

5. Arrest the beam and pans before placing anything upon the latter or removing anything from them.

6. Place the object to be weighed and the larger weights in the middle of the pans. If the terminal knife edges are parallel with the central one, and if there is no considerable friction either upon them or in the jointed hook or chain by which the pans are suspended from the stirrups, the weighings will be correct whatever may be the position of the loads upon the pans. The above precaution is nevertheless to be observed, because the placing of a heavy load at a distance from the center causes a somewhat violent displacement of the pan, which is followed by oscillations not easily quieted.

7. See that the rider is not so near the beam as to be hit by it while swinging.

8. All weighings should be made with the balance case closed.

9. If the beam does not begin to swing as soon as it is released, set it in motion by wafting the air over one of the pans with the hand, or by raising and releasing it again.

10. Objects cannot be correctly weighed while hot, owing to the upward air currents which they create about the pans on which they rest. They may also, through their heating effects on the beam, produce a change in the relative lengths of the arms. Neither should objects be weighed while they are colder than the atmosphere of the balance room, since in that condition they may condense moisture on their surfaces.

11. Hygroscopic and volatile substances, also those which absorb carbon dioxide from the air, must be weighed in closed vessels. If the vessels have been tightly closed while warm, there may be diminished pressure within, in which case they must be opened for a moment before weighing.

12. Substances which are exposed to the air condense moisture on their surface to an extent which sensibly affects their weight. The amount of moisture thus condensed varies with the humidity of the atmosphere; hence a substance which is

transferred from a desiccator to the balance pan will gain in weight for a time, while one which is brought from a damper atmosphere than that within the balance case will lose weight. One must therefore assure himself, before regarding an observed weight as final, that the object is neither gaining nor losing from this cause. Powdered and porous substances which have been dried in a desiccator or in a hot-air bath should be weighed in closed vessels, since owing to the great surface which they present to the air they condense large quantities of moisture. By keeping drying agents in the case it is endeavored to maintain a fairly uniform condition of humidity, and thus to reduce the errors arising from the condensation of water upon the surface of the objects weighed. It is a question, however, whether the use of such agents does not, in practice, bring about greater fluctuations of humidity within the balance case than are observed outside of it. If this is true, it would manifestly be of advantage to discard them wherever their presence is not necessary to prevent corrosion, as, for instance, of steel knife edges.

13. An object which, like glass, is likely to become electrified by friction should not be wiped or brushed immediately before weighing. Glass and quartz weights sometimes become strongly electrified when lifted out of their places in the box in which they are kept.

14. Long tubes and other objects not easily centered on the pans should be suspended from the hooks above the pans.

EXERCISE I

PRACTICE WITH THE BALANCE

I. DETERMINATION OF THE TIME OF VIBRATION

(a) Dust the pans, the beam, the knife edges, and their bearings with a camel's-hair brush. Cautiously release first the pans and then the beam. After the beam has oscillated a few



times—long enough to recover from the effects of any jar it may have received when released—determine the time consumed by the pointer in making ten excursions past the central line on the scale. One tenth of this is the *time of vibration*.

(b) Repeat the experiment with long, short, and medium excursions of the pointer.

(c) Determine the time of vibration with loads of five, ten, twenty, thirty, forty, and fifty grams upon each pan.

The time of vibration will be found to vary somewhat with the load. It also varies with the length of the beam, as was stated in a previous paragraph; but with a given length of beam and a given load the time of vibration is a good test of the sensibility of the balance. A marked decrease in time of vibration with increased loads indicates a bending of the beam.

II. DETERMINATION OF ZERO POINTS

(a) Release the balance and, after the pointer has made a few excursions over the scale, begin to note and record the distances from the center of the scale at which the pointer stops and begins to return, estimating to tenths of a division. A large magnifying glass may be used with advantage, especially if the oscillations are rapid. Place the readings to the right in a column marked *R*, and those to the left in another column marked *L*. Take a number of observations, say three or four, on one side, and a number which is greater or less by one on the other. Add the two columns and divide each sum by the number of observations. The results thus obtained represent the mean excursion of the pointer to either side of the center of the scale. Add these together, divide by 2, and subtract the quotient from the greater of the two mean excursions. The result gives the distance from the center of the scale—on the side of the longer swings—at which the pointer would stop if the beam were to come to rest, i.e. the zero point.

Example

<i>L</i>		<i>R</i>	
3.8 divisions		3.5 divisions	
3.6 "		3.3 "	
3.4 "		2) <u>6.8</u>	
3) <u>10.8</u>		3.4, mean excursion <i>R</i> .	
3.6, mean excursion <i>L</i> .			

$\frac{3.6 + 3.4}{2} = 3.5$, one half of the total mean excursion, which taken from 3.6, mean excursion to the left, gives the zero point 0.1. The pointer will come to a rest one tenth of one division to the left of the middle line on the ivory scale. It will be seen that, if any two successive readings, as *L* 3.8 and *R* 3.5, or *L* 3.6 and *R* 3.3, or successive pairs of readings, as *L* 3.8, 3.6 and *R* 3.5, 3.3, had been treated in the same way, the zero point would have been located at 0.15 of a division to the left instead of 0.1. The first method is obviously the more correct, since it takes into account the fact that the excursions become shorter and shorter in consequence of friction on the knife edges and the resistance of the air.

If the zero point is found to be more than one half of one division to the right or the left of the middle line on the scale, an examination should be made to ascertain whether the displacement may not be due to the accumulation of dust on the beam or pans. If it is not, — that is, if it persists after a careful dusting of the balance, — it is probably the result of corrosion, and the zero point should be adjusted to its proper position by means of the arrangement for that purpose which is to be found on every balance. Exact adjustment, however, is useless, since, as chemical balances are usually located, the relative lengths of the arms — and consequently the zero points — are constantly changing. A slight displacement of the zero point may be due to the fact that the balance is not level.

(b) Repeat experiment (a) with long, short, and medium excursions of the pointer. The zero points should remain nearly constant.

(c) Determine the zero point every fifteen minutes for an hour.

If the zero points are found to vary regularly in one direction, or for a time in one direction and then in the other, it is probable that the ratio of the arm lengths is changing in consequence of unequal changes of temperature.

Lack of constancy in a series of zero points may also be due to dust between the knife edges and their bearings, to the defective condition of the same resulting from wear, rust, or imperfect workmanship, or to the jarring of the balance. If it is due to dust, wear, or to rusted knife edges, the irregularity will generally be found to be in some way related to the length of the swings employed in determining the points. But whether any relation of this kind can be discovered or not, the working parts of the balance should be carefully brushed and the knife edges and their bearings should be examined with a magnifying glass. The stability of the foundation on which the balance rests should also be tested by placing on it or within the balance case the mercury bottle previously mentioned. Lack of constancy in the loaded balance may be due to the unequal bending of the two arms.

III. DETERMINATION OF SENSIBILITY

Strictly speaking, the sensibility of a balance is the angle through which the beam will turn for a given small load upon one side when there is no corresponding counterpoise upon the other. In ordinary parlance it is the displacement of the zero point, in scale divisions, which is produced by adding to or subtracting from the burden borne by one of the arms a weight of one milligram.

(a) Determine the zero point of the balance without load. Place the rider on the one-milligram division of the graduated arm and again determine the zero point.

The distance between the two points is the sensibility. The true sensibility, i.e. the angular displacement of the beam

produced by one milligram, can be calculated if the length of the pointer and the width of the scale divisions are known. Other things being equal, i.e. length of beam, weight of beam and pans, and friction, the sensibility depends on the nearness of the center of gravity to the beam axis. A balance is sufficiently sensitive for ordinary quantitative work when the addition of one milligram to either side will move the zero point from two to three divisions of the scale. For more delicate work, such as the determination of atomic weights, the center of gravity is raised until the same difference of load will give a deflection of six or seven divisions. With a sensibility of two and a half or three divisions, $\frac{1}{20}$ milligram can be weighed with a fair degree of certainty, while a sensibility of five or six divisions will enable one to detect differences of weight amounting to not more than $\frac{1}{50}$ milligram. The adjustment of the sensibility of a balance should not be undertaken by inexperienced persons.

(b) Remove the rider, place five grams upon each pan, and determine the zero point. Replace the rider on the one-milligram division of the arm and again determine the zero point. Repeat the experiment with loads of ten, fifteen, twenty, twenty-five, thirty, forty, and fifty grams upon each pan.

If the terminal knife edges are below the central one, the sensibility will rapidly decline with increasing loads. Any bending of the beam will, of course, produce the same result. If the knife edges are in bad condition, the sensibility will also decline with increasing loads in consequence of undue increase of friction.

If the three knife edges are in the same plane, or if the terminal knife edges are above the central one, the center of gravity will rise when the loads upon the pans are increased, and the balance might therefore be expected to exhibit greater sensibility. But any advantage from this source is usually somewhat more than offset by the loss of sensibility which results from the augmentation of the mass to be moved in the operation of weighing, i.e. beam, pans, and loads, and from the

bending of the beam. Hence, as a matter of fact, most balances become less sensitive when heavier loads are placed upon the pans. If a balance exhibits a reasonably uniform sensibility up to a given load and then a sharp decline for greater burdens, it is certain that the beam is bending under the heavier weights, and that the limit to which it ought to be loaded has been reached.

There are two methods of securing constant sensibility in balances, i.e. a sensibility which does not vary with the weight to be determined. One of them was first employed by Verbeek and Peckholdt and the other by Bunge. The former enhance the increase of sensibility resulting from the rise of the center of gravity when additional loads are placed upon the pans by fixing the terminal knife edges above the central one and, by exact adjustment, make the gain from this source just equal to the loss of sensibility from all other causes. The adjustment must, of course, be such that the maximum load for any balance can neither throw the terminal knife edges below the central one nor raise the center of gravity so high as to produce indifferent equilibrium.

In Bunge's balance of constant sensibility the arms are of different length and weight, and only the shorter and lighter one is supplied with a pan. This difference in the length and weight of the two arms is so regulated that the maximum weight which the balance is intended to carry, say 200 grams, just suffices to bring the beam into equilibrium. The object to be weighed is placed upon the pan and weights are added until the balance is brought to a state of equilibrium. The difference between the weight which is known to produce equilibrium and the sum of the weights placed on the pan is the weight of the object. It will be observed that the balance always carries the same load, and that for this reason its sensibility is constant.

Any balance of ordinary construction can be used as an instrument of constant sensibility in the following manner: A tare of suitable character, which is heavier than the heaviest

object to be weighed, is placed upon one of the pans. The object to be weighed is placed upon the other pan and weights are added until the beam is in equilibrium. The object is then removed and more weights are added until the beam is again in equilibrium. The difference between the weights necessary to produce equilibrium on the two occasions is the weight of the object. This method of weighing with the ordinary balance is an excellent one, since it offers the double advantage of constant sensibility and elimination of errors due to an unequal or variable ratio of arm lengths.

The distance between the center of gravity and the beam axis varies somewhat with the temperature, shortening in cold and lengthening in warm weather. Hence a balance with a given adjustment is found to be more sensitive in winter than in summer, and it sometimes happens that a balance which has been adjusted to great sensitiveness in hot weather exhibits indifferent equilibrium in very cold weather.

IV. TO DETERMINE WHETHER THE ARMS ARE EQUAL

(a) Determine the zero point of the empty balance. Place a one-milligram weight on the right-hand pan and determine the zero point. Transfer the weight to the other pan and again determine the zero point. If the arms are of the same length, the last zero point will lie as much to the right as the second does to the left of the first.

This test is decisive only when the balance is very sensitive and the knife edges and their bearings are in good condition.

(b) Determine the zero point of the empty balance. Place a ten-gram weight upon each pan and determine the zero point. Exchange the weights and again determine the zero point.

If the arms are equal and the weights are equal, the second and third zero points will coincide with the first. If the arms are equal and the weights unequal, the second and third zero points will deviate equally to the right and left of the first. If the

arms are unequal and the weights equal, the second and third zero points will coincide with each other, but not with the first. If both arms and weights are unequal, the second and third zero points cannot coincide with each other, neither can they deviate equally to the right and left of the first. It follows that if the second and third zero points coincide with the first, or if they deviate equally to the right and left of it, the arms are of equal length. Any other relation of the three points indicates inequality. Of course any slight difference in the length of the arms may escape detection by this, as by all other methods, if the knife edges or their bearings are in bad condition.

As has been stated already, the exact ratio of the arm lengths is of little concern to the chemist, since, whatever the ratio may be, if it remains constant, his weighings are relatively correct, and this suffices for most purposes. The ratio, if known, may be utilized to correct weighings; but as a matter of fact it is not so used, because, first, being changeable, it must be redetermined for every new experiment; and, second, there are easy methods of weighing which eliminate the errors resulting from the inequality of the arm lengths.

The ratio is ascertained by weighing an object, usually a brass weight, first upon one pan and then upon the other. Any apparent difference of weight found by the two operations is due to the inequality of the arms. The procedure is as follows.

Determine the zero point of the empty balance. Place a ten-gram weight upon each pan, representing them by P and P' respectively. Determine the zero point and the sensibility of the balance with the weights upon the pans, and calculate what weight must be added to or subtracted from P to produce equilibrium, i.e. to make the zero point coincide with that of the empty balance. Exchange P and P' , and, in the same manner as before, find how much, plus or minus, must be added to P to produce equilibrium. Let p represent the weight which must be added when P is on the left pan, and p' that which

must be added when P is on the right pan. Let R and L represent the length of the right and left arm respectively. Then

$$L(P + p) = P'R,$$

and

$$LP' = (P + p')R.$$

Multiplying together the corresponding terms,

$$L^2P'(P + p) = R^2(P + p')P'.$$

Dividing by P' , $L^2(P + p) = R^2(P + p')$,

or
$$\frac{L}{R} = \sqrt{\frac{P + p'}{P + p}}.$$

Dividing numerator and denominator of the second term by P ,

$$\frac{L}{R} = \sqrt{\frac{1 + \frac{p'}{P}}{1 + \frac{p}{P}}}.$$

Extracting the square root of numerator and denominator separately, we have, approximately,

$$\frac{L}{R} = \frac{1 + \frac{p'}{2P}}{1 + \frac{p}{2P}}.$$

Dividing numerator by denominator,

$$\frac{L}{R} = 1 + \frac{p' - p}{2P}.$$

EXERCISE II

PRACTICE IN WEIGHING

I. WEIGHING BY THE USUAL METHOD

(a) Determine the zero point of the empty balance. Place the object to be weighed — a crucible, coin, or something else which does not change its weight in the air — in the center of the left-hand pan, and the weights which are supposed to be about equal to it in the center of the right-hand pan. Slowly release the balance — pans first, and then the beam — until it is seen which way the pointer turns, and then, as slowly, arrest it again. Add or remove weights, as may be required, and again release and arrest the beam as before. Repeat these trials, using the rider for weights under a centigram until the zero point is found to coincide with that of the empty balance.

(b) Proceed as directed under (a) until it is found that not more than one milligram must be added to or taken from the weights in order to produce equilibrium, and then determine the zero point. Add or subtract one milligram by moving the rider along the beam and again determine the zero point.

The last operation gives the sensibility of the balance for the load which is upon the pans, and from this is to be calculated what weight is to be added or subtracted in order to produce equilibrium.

Example

Suppose the zero point of the empty balance is 0.5 division to the left of the middle line on the scale, and the zero point when the weights nearly balance the object is 1.0 to the right, while the sensibility is 3.0 divisions. It is clear that the addition of one half milligram to the weights already in the balance will produce equilibrium, since that is the weight required to move the zero point 1.5 divisions, i.e. from 1.0 right to 0.5 left. Of the two methods, (a) and (b), the latter is the better, and it should be generally employed in quantitative work.

Instead of determining the sensibility of the balance each time a weighing is made, one may utilize, in the form of a table or a curve, the sensibilities for different loads as determined in Exercise I, III. This course, however, is not to be recommended, since it is not safe to assume that the sensibility has not changed in the meantime. It will be seen that balances of constant sensibility have this distinct advantage over others, namely, that all weights less than a milligram can be read directly from the scale.

It is assumed, whenever either of the methods (a) or (b) is employed, that the arms are of equal length, whereas they are usually to some slight extent unequal. But no harm results from this assumption if, as in ordinary analytical work, it is only necessary that the various weighings shall be correct with respect to each other; and they are thus relatively correct, however unequal the arms may be, provided the ratio of the arm lengths does not change. If the ratio of the arm lengths were known, the errors in weighing due to inequality could be corrected; but corrections of this sort are seldom undertaken because the ratio is not constant. It varies in consequence of unequal changes of temperature and also because of unequal bending under the strain of the loads upon the pans. If the work to be done is of such a character that the errors in weighing due to inequality or varying ratio of the arm lengths cannot be neglected (i.e. if exact weighings are required rather than those which are correct with respect to each other), one of the two following methods is employed. Both eliminate the errors due to the inequality and to the changeable ratio of the arms.

II. WEIGHING BY THE METHOD OF BORDA

(a) Determine the zero point of the empty balance. Place the object to be weighed upon the right-hand pan and balance it to within one milligram by placing weights upon the left-hand pan. Determine the zero point and the sensibility, and

from these calculate how much would have to be added to or subtracted from the weight of the object to produce equilibrium, i.e. to make the zero point coincide with that of the empty balance. Remove the object and put weights in its place until equilibrium is nearly obtained. Again determine the zero point and calculate from the sensibility how much must be added to or subtracted from the weights on the right-hand pan in order to produce equilibrium.

Let P represent the unknown weight of the object, p the weights, plus or minus, which must be added to P to produce equilibrium, W the weight on the right-hand pan, and p' the weight, plus or minus, which must be added to W in order to produce equilibrium.

Now, since $P + p$ and $W + p'$ both balance the load on the left-hand pan, they are equal to each other, and $P = W + p' - p$. The proper algebraical sign must be given to p and p' .

This procedure is also called the method of weighing by substitution.

(b) Place upon the left-hand pan something which is heavier than the object to be weighed. A weight or a small beaker containing shot will answer the purpose. Put the thing to be weighed upon the right-hand pan and add weights until equilibrium is obtained. Remove the object and add more weights until equilibrium is again obtained. The difference between the weights required in the two cases is the weight of the object.

It will be seen that the principle involved in this method is identical with that on which Bunge's balance of constant sensibility is constructed.

III. WEIGHING BY THE METHOD OF GAUSS

Weigh the object as directed in Exercise II under II (b) first on one pan and then on the other. Multiply the two weights together and extract the square root of the product.

Let W represent the true weight which is to be found, A the weight which is found when the object is on the right-hand pan, B the weight obtained when it is on the left-hand pan, R the length of the right arm, and L the length of the left arm.

We then have

$$WR = AL,$$

$$WL = BR,$$

$$W^2 RL = ABRL,$$

$$W^2 = AB,$$

$$W = \sqrt{AB}.$$

Half the sum of A and B may be taken as the true weight whenever the difference between $\frac{A+B}{2}$ and $\sqrt{AB}$ is too small to be detected by the balance.

IV. CORRECTION FOR THE AIR DISPLACED

Just as objects which are weighed under water lose weight by an amount equal to the weight of the water which they displace, so those weighed in the air are lighter than they would be in a vacuum by the weight of the displaced air.

Suppose two ten-gram brass weights which have been found to balance each other in a vacuum are again compared in the air. They will be found to balance each other with the same precision as before; for, having the same specific gravity, their volumes are equal and they must therefore lose equally by the transfer. Suppose, on the other hand, that one of the two ten-gram weights which balance each other in a vacuum is made of brass and the other of platinum. If these are compared in the air, they will no longer be found to be equal; for, having different specific gravities, their volumes are unequal, and they must therefore lose unequally by the transfer. The brass weight, having a specific gravity of 8.4, has a volume of 1.19 cubic centimeters; while the platinum weight, with a specific gravity of 21.5, has a volume of only 0.465 cubic centimeter. The average weight of a cubic centimeter of air is 1.2 milligrams. The brass weight will therefore lose in the air 1.428 milligrams,

while the platinum weight will lose only 0.558 milligram. The former will appear to be lighter than the latter by the difference between 1.428 and 0.558, i.e. by 0.87 milligram. In the same way it may be shown that a piece of quartz weighing ten grams in a vacuum would appear in the air to weigh 9.99887 grams if weighed with brass weights, and only 9.99602 grams if weighed with platinum weights; also that the error in weighing a liter of water in the air amounts to more than a whole gram whether the weights are of brass or of platinum.

It appears that weighings conducted in the air are correct only when the object weighed and the weights have the same specific gravity, and that when the two—the object weighed and the weights—differ largely in respect to specific gravity, the errors arising from the buoying effect of the air are too large to be neglected.

To find the true weight of an object weighed in the air, it is clear that we must add to or subtract from its apparent weight the difference between the weights of the air displaced by the object and by the weights. If the object has a smaller specific gravity (i.e. a larger volume) than the weights, this difference must be added; otherwise it must be subtracted.

The volumes in cubic centimeters of the object weighed and of the weights—and consequently of the air displaced by each—are found by dividing their apparent weight (weight in air) in grams by their respective specific gravities. Strictly speaking, the method is slightly erroneous because the weights found in the air are not true weights, and the calculated volumes are therefore not quite the true volumes. In a few cases this error may require correction, as, for example, in weighing a liter of water, in which instance it amounts to something over a milligram.

Let W represent the true weight of an object (i.e. its weight in a vacuum), P its apparent weight (i.e. its weight in the air), d the specific gravity of the object, d_1 the specific gravity of the weights, and a the weight of one cubic centimeter of air at the

time of weighing. Then we have as a general formula for the corrections of weighings made in the air

$$W = P + Pa \left(\frac{1}{d} - \frac{1}{d_1} \right).$$

The weight of a cubic centimeter of air varies with the pressure, the temperature, and the latitude, also with the moisture and the carbonic acid which it contains; but for all ordinary corrections of this kind, a is assumed to have a value of 1.2 milligrams, and the equation accordingly becomes

$$W = P + P \cdot 0.0012 \left(\frac{1}{d} - \frac{1}{d_1} \right).$$

$d_1 = 8.4$ when the weights are of brass,

21.55 " " " " " platinum-iridium,

21.50 " " " " " platinum,

2.65 " " " " " quartz,

2.60 " " " " " aluminium.

If, as happens in nearly all weighing operations, weights of two different materials are used, a correction for each must be applied. Suppose, for example, it is desired to find the true weight of a porcelain vessel (specific gravity 2.29) which balances in the air 15 brass grams and 5 platinum decigrams. The formula for the corrections would then become

$$\begin{aligned} W &= 15.5 + 15 \times .0012 \left(\frac{1}{2.29} - \frac{1}{8.4} \right) + .5 \times .0012 \left(\frac{1}{2.29} - \frac{1}{21.5} \right) \\ &= 15.506 \text{ grams.} \end{aligned}$$

A table will be found in Landolt-Boernstein's *Physikalisch-Chemische Tabellen*, 2. Auflage, page 10, which gives the computed values of $0.0012 \left(\frac{1}{d} - \frac{1}{d_1} \right)$ between $d = .7$ and $d = 22$ for $d_1 = 8.4$ (brass weights), $d_1 = 2.65$ (quartz weights), and $d_1 = 21.55$ (platinum weights containing ten per cent of iridium).

The first chemist to adopt the practice of correcting weighings for air displacement was Edward Turner (1796-1837).

Problem

16.13161 grams of zinc gave 20.08608 grams of zinc oxide. 14 grams of the metal and 15 grams of the oxide were weighed with brass weights, and the remainders with platinum. The specific gravity of zinc is 7.15 and that of the oxide 5.65; what were the true weights of the metal and of the oxide? If the atomic weight of oxygen is 16, what is that of zinc?

Weighing by Tares

The accuracy of weighings may be considerably increased by employing as counterpoises for the vessels in which substances are weighed (such as flasks, crucibles, tubes, etc.) other vessels of the same material, form, size, and weight. The advantages of so doing are: (1) the vessels and their tares being of the same material and presenting the same area of surface to the air, condense or absorb the same amount of moisture, and the weighings are thus freed to a great extent from the errors which arise from the varying humidity of the atmosphere; (2) having the same density, no corrections for air displacement are necessary; (3) any errors resulting from changes in the weight of the vessel (due to heating, immersion in liquids or vapors, or to other necessary treatment) may be avoided by subjecting the tare to precisely the same treatment.

In practice, the lighter of the two vessels, the weights of which should be very nearly equal to begin with, is selected as the tare; and to this fragments of the same kind of material are added until the vessels do not differ in weight more than a fraction of a milligram. The difference in their weights is then carefully determined by means of the displacement of the zero point which it produces and the sensibility of the balance, and allowance is made for it in all subsequent weighings.

EXERCISE III

CORRECTION OF WEIGHTS

I: COMPARISON OF THE DIFFERENT PIECES OF A SET WITH EACH OTHER

Wherever there are two nominally equal weights in the set, mark one of them by making a slight indentation upon it with a piece of steel having a smooth point. Such stamped weights will be designated in what follows by the letter *s*. Determine the zero point of the empty balance. Place the one-gram weight upon one pan and the fractional pieces nominally equal to it on the other. Determine the zero point and the sensibility of the balance, and from these calculate the difference between the two loads. Reverse the loads and again find their differences in weight in the same manner. Find their true difference in weight by the method of Gauss. Regard the one-gram piece as the standard weight and the difference between it and the sum of the fractional pieces as the error of the latter. To determine the value of the larger weights as compared with the standard, make the following weighings.

2^s against 1 plus the fractional weights, assigning to the latter their true value as compared with 1,

2	against 2 ^s ,	
5	"	$2 + 2^s + 1,$
10 ^s	"	$5 + 2 + 2^s + 1,$
10	"	$10^s, \text{ also against } 5 + 2 + 2^s + 1,$
20	"	$10 + 10^s, \text{ also against } 10^s + 5 + 2 + 2^s + 1,$
50	"	$20 + 10 + 10^s + 5 + 2 + 2^s + 1.$

It remains to be discovered how the error of the sum of the fractional weights is distributed among the several pieces. Weigh 0.010^s against 0.005 + 0.002 + 0.002 + 0.001. Regard 0.010^s as the standard fractional weight, and the difference between it and the smaller pieces as the error of the latter.

To find the value of the larger fractional pieces, weigh:

0.010	against	0.010 ^s ,
0.020	“	0.010 + 0.010 ^s ,
0.050	“	0.020 + 0.010 + 0.010 ^s + 0.005 + 0.002 + 0.002 + 0.001,
0.100 ^s	“	0.050 + 0.020 + 0.010 + 0.010 ^s + 0.005 + 0.002 + 0.002 + 0.001,
0.100	“	0.100 ^s ,
0.200	“	0.100 + 0.100 ^s ,
0.500	“	0.200 + 0.100 + 0.100 ^s + 0.050 + 0.020 + 0.010 + 0.010 + 0.005 + 0.002 + 0.002 + 0.001.

Having thus found the value of the fractional pieces above 0.005, as compared with 0.010^s, bring them all to the standard of the larger weights, the one-gram piece, by correcting each for its share of the total error (i.e. the difference in weight between the sum of the fractional pieces and the standard one-gram weight). In making this correction, 0.005, 0.002, 0.002, and 0.001 will, of course, be regarded as a single weight. If the arms of the balance are so graduated that ten full milligrams can be added to them by means of the rider, as in the Becker balance, it is not necessary to carry the comparison of the weights below the 10-milligram pieces. If the arm is divided into only ten equal parts, and the construction of the beam is such that the rider cannot be carried quite to the terminal knife edges, it is necessary to begin the work upon the fractional weights by weighing 0.005 against 0.002 + 0.002 + 0.001. The value of the riders is found by weighing them against a corrected 0.010-gram piece. If only one arm of the balance is graduated and the riders weigh twelve milligrams each, it will be necessary, in order to obtain weighings on both sides, to weigh the riders against 0.010 + 0.002. In this case the correction of the weights must be extended so as to include the milligram pieces.

Having found the values of the various weights with respect to the one-gram piece, any other weight in the set may be made

the standard of comparison. Suppose it is desired to find the value of the various weights with respect to the stamped ten-gram piece.

Let x represent the value of any weight as compared with the new standard (i.e. the value to be found), a the value of the same weight as compared with the one-gram piece, and b the value of 10^s as compared with the one-gram piece.

The equation for finding the value of x will then be

$$b : 10 :: a : x, \text{ or } x = 10 \frac{a}{b}.$$

II. TO COMPARE A SET OF WEIGHTS WITH A STANDARD WEIGHT

Find the difference between the standard and the piece of the same nominal weight in the set by the method of Gauss. Compare the weights with each other and find, in the manner prescribed under I, the value of each piece with respect to the standard weight.

As a rule, the balances of a chemical laboratory are so unfavorably located and so destitute of the accessories required for refined weighing, that it is difficult to make satisfactory comparisons of weights with them. Fortunately, however, the adjustment of weights has been carried by several makers to a very high degree of precision, and the weights which are furnished by them need not be tested unless the work to be done demands very great accuracy.

Materials for Weights

The substances commonly employed as material for weights are brass, platinum, platinum-iridium, quartz, and glass. Brass is inexpensive and is easily formed and adjusted, but is too readily corroded. This defect, however, is often remedied by gold plating the weights. Platinum is noncorrodible and readily adjusted, but it is too costly and has a specific gravity too far

above that of a majority of the substances commonly weighed. Quartz and glass are not easily attacked by substances likely to find their way into the air, and they have specific gravities quite near to those of many of the substances to be weighed ; they are, however, in consequence of their greater hardness, more difficult than the metals to fashion and adjust, and the weights made from them easily become electrified when they are removed from their places in the box, especially when the box is lined with velvet or leather.

CHAPTER II

THE BAROMETER AND THE THERMOMETER

THE BAROMETER

The principal use of the barometer in a chemical laboratory is in connection with the measurement of gases and the determination of the boiling points of liquids. The instrument usually employed is either the Fortin modification of the *cistern* barometer or the so-called *siphon* barometer.

The simplest form of the cistern barometer consists of a wide vessel, the *cistern*, and a long glass tube closed at one end and open at the other. The tube is filled with mercury, inverted, and its open end immersed in mercury which partly fills the cistern. The pressure of the air is then measured by the height to which the mercury rises in the tube, i.e. by the vertical distance between the upper surfaces of the mercury in the cistern and in the tube. The principal objection to this form of the instrument is the necessity of employing either an adjustable scale, or — if fixed — one so contrived as to compensate for the difference between the cistern and the tube in respect to cross section. In the Fortin barometer, Fig. 1, this difficulty is obviated by employing a cistern having a flexible leather bottom which can be raised or lowered by means of an adjusting screw placed underneath. By this means, whenever a reading is to be taken, the level of the

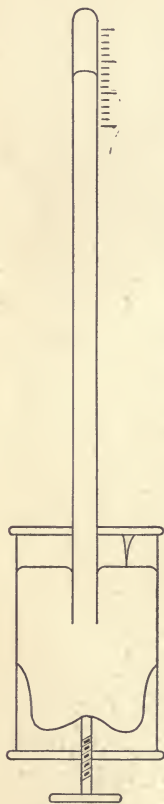


FIG. 1

mercury in the cistern is made to coincide with the lower extremity of the graduated scale upon or at the side of the barometer tube. The correct adjustment of the surface is made possible

by a sharp-pointed ivory indicator, which is fixed in a vertical position above the mercury in the cistern in such a manner that its lower, pointed end lies in the same horizontal plane with the lower extremity of the graduated scale. The slightest contact between the ivory point and the metal produces a visible depression in the surface of the latter. The scale may be etched upon the tube, but it is usually of brass and is often provided with a vernier, Fig. 2, and with accessories designed to obviate those errors in reading which are due to parallax.

The siphon barometer, Fig. 3, is so called with reference to its form only. It consists of a U-shaped tube having one limb much longer than the other. The long limb is closed at the top and bent so as to bring its upper portion into line with the shorter limb. The scale is usually etched upon the glass and extends over both limbs. The point from which the enumeration of the divisions of the scale begins may be above the highest or below the lowest possible level of the mercury in the shorter limb. In the former case the numbers increase in the upward direction on the longer and in the downward direction on the shorter limb, and the readings on the two limbs are to be added; while in the latter case the numbers increase in the upward direction on both limbs and the readings are to be subtracted.

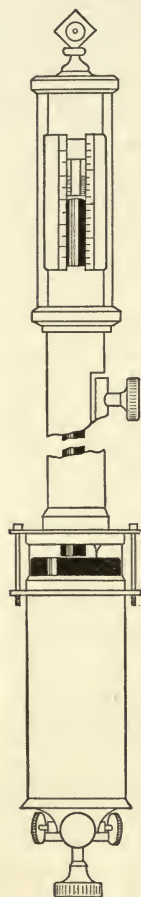


FIG. 2



FIG. 3

There are certain facts concerning the barometer and its use which require attention.

1. The mercury must be pure in order that its density may be normal and its movements in the tube free.

2. The tube of a cistern barometer must be of sufficient internal diameter ; since, otherwise, the height of the mercury column is sensibly affected by capillary depression. In the siphon barometer this difficulty disappears except in so far as the meniscuses in the two limbs of the instrument differ in form owing to the fact that one of them is in the air and the other in a vacuum.

3. The inclosed space in the tube above the mercury must be free from air and moisture. The simple filling of a tube with mercury does not completely remove the air. A small portion of it clings to the glass and this can be expelled only by boiling the mercury in the tube ; hence all barometers are "boiled out" at the time of filling. Whether the inclosed space is free from air or not may be ascertained by tilting the instrument to one side until the mercury rises to the top of the tube, when, if air is absent, the mercury will fill the entire space. Another way of testing for the presence of air is cautiously to set the column of mercury in motion until it strikes against the top of the tube. If the vacuum is complete, a sharp ringing sound will be produced which is unmistakable.

The depression of the barometer which is produced by the vapor of the mercury itself is insignificant, amounting at 20° only to 0.02 mm.

4. The scale by which the height of the barometer is read, if not known to be correct, must be tested. This may be done with sufficient accuracy for most purposes in the following manner. A pair of slender sharp-pointed dividers with screw adjustment are opened on any part of the graduation until some whole number of divisions, e.g. ten, are included between the points. Thus adjusted, the dividers are run several times over the whole scale, beginning each time at a new place. If the points are always found to span the same number of divisions, the graduation is sufficiently uniform, and it remains only to ascertain whether it is sufficiently correct. The latter

question is quickly settled by placing the dividers, without alteration of adjustment, upon a scale known to be correct, which should be of the same material as that under examination.

5. The barometer, when read, must have a vertical position, and care must be taken to avoid errors of parallax. If practicable, a telescope should be employed.

6. The siphon barometer should be gently tapped before reading in order to overcome a tendency on the part of the mercury to lag in its movements in the tube. This treatment is not necessary in the case of the Fortin barometer when the column has been set in motion by the adjustment of the level of the mercury in the cistern.

CORRECTIONS OF THE BAROMETER

I. For Temperature

Since the density of mercury decreases with rising temperature, the height of the column supported by a given atmospheric pressure will vary somewhat with the temperature of the air (e.g. the pressure which supports a column 760 mm. high at 0° will, at 20° , support one 762.76 mm. in length). It is necessary, therefore, to select some standard temperature for the mercury and to correct accordingly all readings made at other temperatures. The standard temperature is 0° , and the term "height of the barometer" signifies not the observed height but that which it would have at 0° . Since the height of the column of mercury supported by the weight of the air is, in general, independent of the diameter of the tube, the corrected height (b) will be found by dividing the observed height (b') by unity plus the cubical expansion of mercury ($0.0001818 t$) from 0° to the temperature at which the reading was made. The general

formula for the correction is $b = \frac{b'}{1 + 0.0001818 t}$, when the tem-

perature is above 0° ; and $b = \frac{b'}{1 - 0.0001818 t}$, when the temperature is below 0° .

The effect of change in temperature upon the length of the scale must also be taken into account, for its graduation is correct only at the standard temperature of 0° . Obviously the divisions are too far apart at temperatures above 0° , and too near together at temperatures below that point. If b and t have the same significance as in the previous formulas, while γ represents the linear-expansion coefficient of the material of the scale, the formula for the correction of the scale is $l = b(1 + \gamma t)$, or $l = b(1 - \gamma t)$, according as the temperature is above or below 0° at the time of reading.

Letting h represent the true height of the barometer, we have, by combining the two corrections, the formulas

$$h = b' \frac{1 + \gamma t}{1 + 0.0001818 t}$$

for temperatures above 0° , and

$$h = b' \frac{1 - \gamma t}{1 - 0.0001818 t}$$

for temperatures below 0° .

$\gamma = 0.0000085$ when the scale is of glass, and 0.0000184 when it is of brass.

It will be observed that the two errors — the one due to change in the density of the mercury and the one due to change in the length of the scale — tend to compensate each other at all temperatures.

Simpler formulas for the temperature correction of the barometer which, though not entirely accurate, are sufficiently so for most purposes, are :

$h = b' (1 - (0.0001818 - \gamma) t)$ for temperatures above 0° ,
and $h = b' (1 + (0.0001818 - \gamma) t)$ for temperatures below 0° .

These become

$$h = b' (1 - 0.0001733 t) \text{ and}$$

$$h = b' (1 + 0.0001733 t) \text{ when the scale is of glass,}$$

$$\text{and } h = b' (1 - 0.0001634 t) \text{ and}$$

$$h = b' (1 + 0.0001634 t) \text{ when the scale is of brass.}$$

II. For Capillary Depression

As previously stated, there is no correction to be made for capillary depression in the siphon barometer. The depression is likewise negligible in cistern barometers when the diameter of the mercury column is equal to or exceeds 25 mm. In narrower tubes, however, the depression sensibly affects the height of the barometer, and is to be added to the readings of the instrument unless the correction has already been provided for in the scale itself.

The following table gives the amount of the correction for tubes of various small diameters.

DIAMETER OF TUBE	DEPRESSION	DIAMETER OF TUBE	DEPRESSION
4 mm.	1.64 mm.	14 mm.	0.12 mm.
6 "	0.91 "	16 "	0.07 "
8 "	0.54 "	18 "	0.04 "
10 "	0.32 "	20 "	0.03 "
12 "	0.19 "		

III. For Latitude and Altitude

The atmospheric pressure which will support a column of mercury of given height, e.g. 760 mm., is not a fixed quantity, but diminishes as the distance from the earth's center of gravity increases. It varies, therefore, with latitude and elevation above sea level. Hence it is necessary, even for meteorological comparisons, to establish a unit for the earth's attraction and to reduce observations on the height of the barometer in all parts of the earth's surface to this standard. The unit agreed upon is the force of gravity which is found to prevail at sea level in latitude 45° . If it is desired to reduce a reading of the barometer made at any other latitude and altitude to the height which it would have — with the same atmospheric tension — at latitude 45° and sea level, the observed height, corrected for temperature, is to be multiplied by the expression

$$(1 - 0.0026 \cos 2\phi) (1 - 0.0000002 H),$$

in which ϕ is the latitude of the place and H its elevation in meters above sea level. The latter term, $(1 - 0.0000002 H)$, may be neglected except when the altitude of the place is considerable, since at an elevation of 500 meters the correction for altitude amounts to only 0.07 mm.

The following table will give an idea of the magnitude of the corrections for latitude when the observed height of the barometer is 760 mm.

Latitude	=	0°	12°	18°	24°	30°	36°	42°	45°
Correction $\mp$	=	1.97	1.80	1.59	1.31	0.98	0.61	0.21	0.0 mm.
Latitude	=	90°	78°	72°	66°	60°	54°	48°	45°

The correction is subtracted from the height of the barometer, or added to it, according as the latitude of the place of observation is below or above 45°. It will be observed that, with equal atmospheric pressure at the two places, a barometer at the equator would stand 3.94 mm. higher than one at the pole.

What has been said of the mutual relations of barometric height, atmospheric pressure, and the force of gravity is also true of every other column of mercury which is supported by the pressure of a gas or by the difference between two gas pressures. The bearing of this fact upon the work of the chemist will be made clearer by outlining the most common method of measuring a gas. A tube, closed at one end and graduated, is filled with mercury, inverted, and its open end immersed in mercury in an open vessel. The apparatus thus prepared resembles a cistern barometer, and is one, in fact, if the length of the tube is equal to or greater than a barometric height. The gas to be measured, on being introduced into the tube at the open end, rises to the top and depresses the column of mercury. Its volume is then read upon the graduation of the tube. But the term *volume* has no significance in the case of a gas unless the pressure under which it is measured is known, because its volume, leaving temperature out of the consideration, depends on the pressure. Hence it is necessary to ascertain

the pressure resting upon a gas at the time of determining its volume. This is a very simple matter; for, evidently, the pressure upon the gas which determines the space it can occupy is the difference between the pressure of the air and the pressure of the column of mercury in the eudiometer, and this will be found by subtracting the height of the column of mercury in the tube from the height of the barometer. Stated in another way, the sum of the pressure exerted by the gas and that exerted by the column of mercury in the eudiometer is equal to the pressure of the atmosphere; and hence, to find the pressure exerted by the gas, we have only to subtract the height of the one mercury column from that of the other. The result is the height of the mercury column which the gas is capable of supporting, and it is the measure of its pressure or tension in the same sense that the height of the barometer is the measure of the pressure or tension of the atmosphere.

Having thus found the volume of a gas when measured under some known pressure, we can calculate what space it would occupy under any other pressure, — for instance, under the conventional *standard pressure*, which is the pressure required to support at 0° a vertical column of mercury 760 mm. in length. Having found its volume under standard pressure, we can find its weight through the known density of the gas.

This procedure for finding the weight of gases suffices for all ordinary purposes; but when great accuracy is required, as in the determination of an atomic weight, it is necessary to take into account the fact already explained that the height of a column of mercury is not an unvarying measure of the pressure which supports it. In other words, it is necessary to multiply the height of the mercury column which expresses the pressure under which the gas was measured by $(1 - 0.0026 \cos 2\phi)$ $(1 - 0.0000002 H)$ in order to find what its height would be in the standard locality, i.e. latitude 45° and sea level. If this correction is neglected, equal volumes of the same gas will be found to have different weights in different parts of the earth.

IV. For the Moisture in the Air

It is sometimes desired to know what portion of the observed height of the barometer or of another mercury column is due to air or gas in the dry condition. This is found by subtracting from the observed height of the column the *tension* of the water vapor expressed in millimeters of mercury. If the gas is saturated, the tension of the water vapor will be known. Otherwise it must be determined.

THE THERMOMETER

Three things are to be ascertained with respect to a thermometer before it can be used with confidence. They are: (1) the position of the upper end of the mercury column when pure water freezes,—its *zero point*; (2) the position of the same when pure water boils,—its *boiling point*; and (3) the inequalities of its bore.

An instrument having the scale upon the glass and without the white opaque background so common in laboratory thermometers is to be preferred for the exercises which follow.

EXERCISE IV

DETERMINATION OF THE ZERO POINT

There are required:

1. A strong test tube, 25×175 mm.
2. A stout platinum wire, 250 or 275 mm. long.
3. Two corks, one of which fits the test tube, and the other large enough to bore for the tube.
4. A beaker, 100×175 mm., or, better, a glass battery jar of approximately the same dimensions.
5. A cover of wood or metal for the jar.
6. A glass tube or copper wire, 8×600 mm.

Bore the smaller cork centrally for the thermometer, and near the outer edge for the platinum wire; and the larger cork for the test tube.

Bend one end of the platinum wire into a ring which fits loosely the inside of the tube (1), and the rest of the wire into a right angle with the ring. This stirrer may also be made from a thin glass rod or tube; or a ring of platinum wire with a short overlap of wire bent to a right angle may be made, and the *standing* end of the wire fused into the end of a glass tube.

Make a similar stirrer for the jar or beaker (4) out of the glass tube or copper wire.

Bore the cover (5) for the cork on the test tube and for the stirrer.

The apparatus ready for use is shown in Fig. 4.

Partly fill the test tube with distilled water and insert the thermometer. The distance between the lower extremity of the bulb and the bottom of the test tube should be somewhat greater than that between the bulb and the side of the tube, and the level of the water should be above the zero point of the thermometer. Move the stirrer up and down and make sure that it does not rub against the bulb at any point.

Fill the outer vessel with a mixture of pulverized ice, or snow, and a little salt; and if the ice is quite dry, add a little water. Place the tube containing the thermometer and the water in position in the larger vessel, and stir from time to time the freezing mixture. The temperature of the water in the inner vessel will fall somewhat below the freezing point before the formation of ice begins. As soon as the thermometer indicates an *under-cooled* condition, stir the water vigorously in order to prevent the formation of coarse ice and to secure a uniform distribution of temperature. The mercury will rise slightly and become stationary, giving the point to be recorded. Remove the test tube from the freezing mixture and resume the

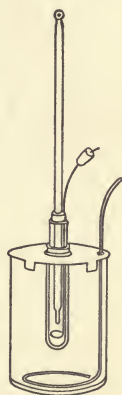


FIG. 4

stirring. The thermometer will remain unchanged until a large portion of the ice has melted. When so much of the ice has disappeared that the thermometer again begins to rise, return the tube to the freezing mixture and repeat the experiment.

Immerse the thermometer bulb in the steam from boiling water for half an hour and then redetermine the zero point.

It will be found that the second zero point is lower than the first. Repeat the heating in steam and again determine the zero point. The second and third results should agree.

It is of some advantage to "jacket" the apparatus with a larger tube, and thus provide an air space between the cooling mixture and the water. The freezing of the water and the melting of the ice are then slower, giving more time for the observation of the thermometer.

A very common but less satisfactory procedure for the determination of the zero points of thermometers will be described. A piece of rubber tubing provided with a pinchcock is attached to the stem of a large funnel, which is placed in the ring of an iron stand and filled with snow or finely powdered ice. The ice, if dry, is then moistened with enough distilled water to expel the air. The bulb of the thermometer, thinly wrapped in flannel to prevent actual contact with the ice, is imbedded in the ice to a point on the stem above the zero mark. From time to time the thermometer is raised, or the funnel lowered, in order to observe the height of the mercury.

There are two objections to this method: (1) the temperature of the ice may be below the freezing point of water, in which case the water in contact with the bulb, despite the flannel covering, may be under-cooled; (2) the ice may contain soluble impurities, which, even in small quantities, sensibly depress the melting point.

The latter difficulty may be avoided in the following manner. A metallic rod of the same diameter as the thermometer is fixed in a vertical position, its lower end immersed in a vessel filled with distilled water, which is afterwards frozen to a solid

cake of ice by surrounding it with a freezing mixture. The rod is loosened by heating its free end, and removed, leaving a cavity for the bulb of the thermometer. The stem of the thermometer is provided with a rubber ring wider than the hole, which rests on the ice when the instrument is in position.

The difference which was observed in the foregoing experiment between the zero points determined before and after heating the thermometer to the boiling point of water is due to the fact that when glass is heated and again cooled to its former temperature it does not immediately shrink to its original volume. In other words, the depression of the zero point which follows a heating of the thermometer is the result of an enlargement of the bulb.

The extent of the depression varies greatly with the composition of the glass, being large in the Thuringian, and small in the so-called Jena normal glass, which contains in addition to the more common constituents of glass — silica, alkalies, and lime — about 7 per cent of zinc oxide and 2 per cent of boric acid. It also varies with the temperature to which the thermometer is heated and with the duration of the heating.

The dilatation is not permanent. The shrinkage of the bulb begins at once; for if a thermometer which has been heated to the boiling point of water is placed in melting ice, the mercury is observed to sink to a certain point, and then slowly to rise. This lowest reading is known as the “zero of maximum depression.” The rate at which the bulb returns to its original volume, like the degree of the dilatation, is variable. The recovery may last a few hours or several months according to the composition of the glass, the temperature to which the thermometer has been heated, the duration of the heating, and the rapidity of the cooling. In the case of new thermometers, a gradual slow rise of the zero point is observed which may require years for its completion.

If a thermometer is heated for a long time to a high temperature, the zero point rises, and in some cases to an astonishing extent. Crafts, after heating certain thermometers of common German and of French crystal glass to 355° for eleven days, observed elevations of the zero points ranging from 11° to 26° . At the same time the intervals between the freezing and boiling points had increased by quantities ranging from 0.45° to 0.9° , showing that the expansion coefficient of the glass had been diminished by the prolonged heating.

The lack of constancy in the position of the zero point—from which temperature is reckoned—does not seriously interfere with the accuracy of the thermometer as an instrument for the measurement of temperature since, in practice, one proceeds in such a manner as to eliminate errors from this source. When a determination is to be made with a thermometer, the instrument is first heated for some time to the temperature which it is afterwards to register, and its zero point then ascertained. Or, what is better, if the heating is a prolonged one, the zero point of the thermometer is determined immediately after the completion of the experiment.

A thin column of mercury moving through a glass tube is considerably retarded by capillary resistance; consequently, at the same temperature, somewhat different readings may be obtained according as the thermometer is observed after a rise or after a fall of the mercury. This effect, known as “stiction,” is especially troublesome in thermometers with very fine threads. It can be overcome to a great extent by jarring the instrument; hence it is customary before reading a thermometer to tap it sharply with one of the fingers, with a piece of hard wood, or—more lightly—with a piece of metal. A very satisfactory device for this purpose is a minute electrical hammer constructed like a vibrating bell, which is attached to the upper end of the thermometer and kept in operation while the mercury is moving up or down to its position of rest.

EXERCISE V

DETERMINATION OF THE BOILING POINT

A metallic vessel constructed on the plan of that represented in Fig. 5 is required. One of the small horizontal tubes serves for the escape of the steam. To the other is attached a glass U-tube partly filled with water to indicate — and to measure if necessary — any difference in pressure between the steam within the vessel and the external atmosphere. The bulb must be above the water in the vessel and the column of mercury should reach only a very short distance above the cork which holds the thermometer in place. In preparing the cork provision is to be made for the passage of steam through it along the stem of the thermometer.

Boil the water rapidly for ten or fifteen minutes; then note the height of the thermometer and any difference in the level of the water in the two limbs of the manometer. Record also the height and the temperature of the barometer.

The temperature at which water boils depends, of course, upon the pressure of the air. The next step, therefore, is to correct the observed height of the barometer to the height which it would have at the standard temperature of 0° , and to correct the true height of the barometer, in turn, for any difference of pressure indicated by the manometer. The reduction of the barometer reading has already been explained. The amount of the second correction is found in the following manner. The temperature of the water in the manometer is ascertained and the density of water at that temperature is found in the appropriate tables. The product of the difference in the level of the water in the two limbs and the density of the water, as found in the appropriate table, is then divided by the density of mercury at 0° , i.e. by 13.5956.



FIG. 5



The pressure found could, of course, be further reduced to its value at latitude 45° and sea level; but, this last refinement would hardly be justified in the case of thermometers which cannot be accurately read to within less than 0.05° , since the effect of a correction for latitude upon the boiling point of water amounts — with a pressure of 760 mm. of mercury — only to 0.037° at latitude 30, 0.025° at 35, and 0.013° at 40. The correction for any moderate altitudes is much smaller, amounting at an elevation of 500 meters only to 0.0026° .

Having found the pressure under which the water was boiled, the temperature corresponding to that pressure, i.e. the true boiling point, may be obtained from the tables. The following table gives the boiling points of water at pressures between 740 and 780 mm. of mercury.

Boiling Points of Water at Latitude 45° and Sea Level

740 99.26°	750 99.63°	760 100.00°	770 100.37°
741 99.30	751 99.67	761 100.04	771 100.40
742 99.33	752 99.71	762 100.07	772 100.44
743 99.37	753 99.74	763 100.11	773 100.47
744 99.41	754 99.78	764 100.15	774 100.51
745 99.45	755 99.82	765 100.18	775 100.55
746 99.48	756 99.85	766 100.22	776 100.58
747 99.52	757 99.89	767 100.26	777 100.62
748 99.56	758 99.93	768 100.29	778 100.65
749 99.59	759 99.96	769 100.33	779 100.69
			780 100.73

Within all ordinary ranges of the barometer a change of 1 mm. in its height affects the boiling point of water 0.0375° .

EXERCISE VI

CALIBRATION OF THE THERMOMETER

There are required :

1. A strip of good mirror glass if the thermometer is a transparent one. Otherwise it cannot be used.

2. A strong magnifying glass, or, better still, a small reading telescope which is mounted on, and movable along, a stationary horizontal rod.

The first step to be taken is the separation of a thread of mercury of suitable length. If the thermometer to be calibrated is one of wide range, e.g. from a few degrees below zero to 360° , as will probably be the case, a thread spanning from 30 to 50 divisions of the scale will suffice.

Invert the thermometer and give it a smart tap against the table top or the palm of the hand. If a thread separates, it will probably be too long or too short. If too long, return the thread nearly to the bottom of the scale and note the position of its lower end. Warm the bulb until the mercury in it rises and joins the thread in the stem, removing the thermometer from the source of heat the moment the junction is established. The cause of the detachment of the thread is a minute bubble of air which is usually located at the point where the stem joins the bulb. If the bulb is subsequently heated, the air bubble is pushed along until the rising mercury joins the thread, when it lodges on the side of the tube and remains attached to the glass in its new position. The next break in the thread will occur at this point. Now cool the bulb until a thread of the right length remains above the place of junction; then invert and tap as before. A thread of the desired length should separate. If it does not, the operation is to be repeated until it is successful.

If, on the other hand, the thread first detached is too short, proceed as before and continue to warm the bulb until a column

of mercury of the right length has risen above the place of junction and then effect the separation in the usual manner.

When a thermometer is inverted and struck against a hard object in the manner described, it frequently happens that the air bubble which is expected to cause the detachment of a thread at the junction of the stem and the bulb glides along the wall of the bulb towards its highest part, while the mercury flows out of the bulb and fills the entire stem. In such cases the bubble is to be brought back to the junction of the stem and the bulb. This can be done by returning the thermometer with a quick movement to the upright position and by tapping the bulb simultaneously against the table. The thread may then be broken off, and shortened or lengthened in the manner described.

The detached thread may be brought with great exactness to any desired position under the graduation by inclining the thermometer and tapping against the ends, but skill in placing the thread can be acquired only by practice.

The correct determination of the position under the scale of the ends of the mercury column is also a matter of some difficulty at first, owing to errors of parallax and to inability to estimate correctly fractions of a division of the graduation. The latter difficulty disappears with practice, but errors of parallax can be avoided only by the employment of suitable means. The best of these is the reading telescope mounted in the manner previously referred to. If this instrument is not to be had, the scale may be observed through a powerful pocket lens which is fixed in a ring supported by three legs. Under such a glass, a line which crosses the optical axis will appear straight, while lines on either side of it will appear to be curved. A weak lens is of little assistance owing to the slightness of the curvature which it gives to lines not crossing its axis. Finally, if the thermometer is a transparent one, it may be mounted on blocks over a strip of mirror glass. The proper position for reading will then be found by bringing the eye, the end of the thread, and its image into line.

Having made the best practicable arrangements for the avoidance of parallax and for magnifying the scale, and having detached a thread of mercury of the desired length, run the thread nearly down to the bulb and place its lower end exactly opposite the scale division at which it is proposed to begin the calibration. Record the position of both ends, and then run the thread up the stem until its lower end exactly coincides with the previous position of its upper end. Record the new position of the upper end. Proceed in this way until the thread has passed through as much of the stem as it is desired to calibrate, and then reverse the operation, running the thread down the stem and recording the succeeding positions of its lower end. The readings while returning should not be compared with those recorded while going up until the work is completed.

On comparing the two records, the readings at corresponding points should be found to agree very closely; though they need not and probably will not be identical if one attempts to estimate very small fractions of a scale division. If the discordance is considerable, it is probably due to the inexperience of the experimenter and the work should be repeated until a satisfactory agreement between the upward and the downward readings is obtained. When readings at corresponding points are found to disagree slightly, the mean of all is to be accepted as probably safer than any single observation.

The errors in reading will tend to accumulate in a single direction; but since one reads in opposite directions, the errors made in going up will neutralize, to a great extent, those made in coming down the stem.

The spaces successively filled by the thread of mercury are spaces of equal capacity or volume, and how these are to be employed in the calibration of the stem will be explained by means of the following example of a first calibration by a student.

A thermometer graduated in whole degrees and ranging from -10° to 360° was placed in steam from boiling water for half an

hour. Immediately afterwards, its freezing and boiling points were determined and found to be located at 2° and 102° respectively.

The height of the barometer corrected was 764.28 mm., which gave for the boiling point of water 100.16° .

A thread spanning 35 divisions in the lower end of the scale was broken off and manipulated up and down the tube in the prescribed manner. The following readings were obtained.

I	II	III	IV	V
UP	DIVISIONS FILLED	DOWN	DIVISIONS FILLED	MEAN OF II AND IV
0.0		0.0		
35.0	35.0	35.0	35.0	35.0
70.2	35.2	70.4	35.4	35.3
106.0	35.8	106.0	35.6	35.7
142.0	36.0	142.0	36.0	36.0
178.2	36.2	178.4	36.4	36.8
215.1	36.9	215.2	36.8	36.9
251.6	36.5	251.8	36.6	36.6
288.0	36.4	288.0	36.2	36.3
324.8	36.8	324.8	36.8	36.8

The whole number of scale divisions filled by the thread when placed nine times end to end was 324.8, while the average number filled was $\frac{324.8}{9} = 36.09$. The thread was therefore

regarded as containing 36.09 volume or calibration units.

The differences between the averages of the corresponding upward and downward readings, and the number of calibration units in the thread, multiplied by 1, 2, 3 . . . 9, gave the corrections to be added at nine points on the scale in order to convert actual into calibrated readings.

VI AVERAGE I AND III	VII CALIB. READINGS	VIII CORRECTIONS
35.0	$36.09 \times 1 = 36.09$	+ 1.09
70.3	$36.09 \times 2 = 72.18$	1.88
106.0	$36.09 \times 3 = 108.27$	2.27
142.0	$36.09 \times 4 = 144.36$	2.36
178.3	$36.09 \times 5 = 180.45$	2.15
215.2	$36.09 \times 6 = 216.54$	1.34
251.7	$36.09 \times 7 = 252.63$	0.93
288.0	$36.09 \times 8 = 288.72$	0.72
324.8	$36.09 \times 9 = 324.80$	0.00

The values in column VIII were then used as ordinates to plot on cross-ruled paper a curve of corrections, the thermometer scale serving as the axis of abscissas.

It will be seen that the calibrated readings in such a curve are correct at certain fixed points, in this case at nine points on the scale; further, that it is assumed that any change in caliber between two adjacent fixed points is uniform throughout the whole of the included space. This assumption is usually incorrect, but the errors resulting from it are not large because they are confined to the particular space in which a reading falls. In other words, errors of this kind do not accumulate from space to space, but cease altogether at the fixed points.

In the case of a thermometer of very irregular caliber it may, however, be desirable to increase the number of correct ordinates for the curve, and thus to diminish the error referred to. To do this, the lower end of the thread is placed about halfway between the first two readings and the calibration is repeated. The number of correctly established points will thus be doubled, and by repeating the process, starting each time from some new point on the scale, the number may be increased to any desired extent.

In order that a thermometer which has been calibrated in the manner described may be used for the correct determination of temperature, it is necessary to ascertain the temperature equivalent of the calibration unit. In the case of the instrument used

as an illustration, the correct readings found on the curve for the freezing and boiling points were 2.20 and 104.2 respectively; i.e. there were 102.0 calibration units included between these two points. But at the time of determining the freezing and boiling points the boiling temperature of water was 100.16°; therefore the temperature equivalent of the calibration unit was

$$\frac{100.16}{102}, \text{ or } 0.98196^\circ.$$

To ascertain the temperature corresponding to any reading of the thermometer, the difference between it and the zero point, in calibration units, is to be multiplied by the temperature equivalent of the unit. When a thermometer is employed to register a high temperature its zero point should be determined *immediately after*, rather than before, the experiment.

Correction for the Exposed Part of a Mercury Column

If a portion of the mercury in the stem of a thermometer is outside of the area whose temperature is sought, the temperature of the exposed part is different from that of the mercury in the bulb. The column is accordingly too short or too long, and requires a correction; i.e. there must be added to or subtracted from its length the amount which it would be lengthened or shortened if the temperature of the exposed part were raised or lowered to the temperature of the mercury in the bulb. The correction to be applied is

$$(t - t')n\gamma, \text{ in which}$$

t is the temperature observed on the thermometer;

t' , the mean temperature of the exposed part of the column, determined by placing another thermometer near its middle point;

n , the length in calibration units of the exposed part; and

γ , the apparent expansion of mercury in glass, i.e. the difference between the cubical-expansion coefficients of mercury and glass, which is 0.0001818 — 0.000025 or 0.0001568.

Obviously t is not exactly the temperature of the mercury in the bulb. The correction is therefore slightly faulty; but any desired approximation to the truth may be secured by substituting for t its corrected value and repeating the calculation.

The temperature of the exposed part of the mercury column cannot be determined with certainty. It is assumed to have the temperature of the medium immediately surrounding the portion of the stem which it occupies, but a little reflection upon the conditions which determine its temperature will convince one that the assumption is not altogether warranted. It is better, therefore, if practicable, to subject the whole column to the same temperature conditions as the bulb rather than to rely on a correction for an exposed fraction of the mercury.

The Comparison of Thermometers

When two thermometers are to be compared, great care must be taken to insure perfectly uniform conditions. They are best compared by placing them in the vapors of boiling liquids. If the comparison is made by immersing them in a liquid, the liquid should be stirred. An air bath is not to be trusted.

Thermometers filled with Gas

When the ordinary thermometer in which there is a vacuum above the mercury is heated nearly to the boiling point of the metal (357°), the column in the stem separates in consequence of the formation of vapor. If, on the other hand, the space is filled with a gas under pressure, the boiling point of the mercury is raised and the thermometer will register much higher temperatures. But progress in this direction is limited by the comparatively low temperatures at which most varieties of glass begin to soften. Within recent years, however, a borosilicate glass with high fusing point has been produced in Jena from which thermometers are made and filled with carbon dioxide

under a pressure of 17 or 18 atmospheres. These thermometers register temperatures up to 550°.

The Beckmann Thermometer

A thermometer much used in the determination of molecular weights by the freezing- and boiling-point methods is that devised by Beckmann, Fig. 35. In this instrument the bulb is so capacious that the entire scale covers not more than five or six degrees, permitting a graduation of the stem to hundredths, and, in some cases, even to thousandths of a degree. In order now that the thermometer may be used for a considerable variety of temperatures, notwithstanding the narrow range of its graduation, a reservoir is placed in its upper end to which any desired portion of the mercury in the bulb may be transferred. It will be seen that the value of a scale division in such an instrument depends on the amount of the mercury left in the bulb. The manner of using the Beckmann thermometer and of correcting its readings, when a portion of the mercury has been removed from the bulb to the reservoir, will be explained in the chapter on the determination of molecular weights.

The Air Thermometer

The simplest form of the gas thermometer, Fig. 6, consists of a glass, porcelain, or platinum bulb connected by means of a capillary tube with a U-shaped adjustable column of mercury.

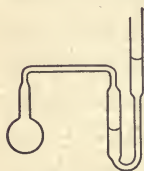


FIG. 6

Its use for the determination of temperature is based on the experience that, with constant pressure, a gas expands very nearly uniformly for equal increments of temperature ($\frac{1}{273}$ part of its volume at 0° for each degree); or, if the volume is constant, the pressure increases in the same ratio.

In practice the volume is kept constant and the temperature is deduced from the pressure. For the measurement of high temperatures the bulb is filled with hydrogen rather

than air because under heavy pressures the former gas obeys the law with greater precision than the latter.

Measurements of temperature by the mercury and by the gas thermometer do not perfectly agree except at the experimentally fixed points, — the freezing and boiling points of water. The reason for the divergence is to be found in the irregularity of the expansion of both mercury and glass. In the mercury thermometer temperatures are measured by the *apparent* expansion of mercury, and this depends, in turn, on the *absolute* expansion of both the metal and the glass, which is not perfectly uniform in the case of either material. Moreover, different varieties of glass exhibit different degrees of irregularity in respect to their expansion coefficients; hence thermometers made from different kinds of glass, though carefully calibrated, will not perfectly agree with one another except at experimentally fixed points.

A difficulty of the same character is experienced in connection with the gas thermometer, inasmuch as the expansion of the material of the bulb as well as that of the gas must be taken into account. The former, however, is so minute as compared with the latter that the mere irregularities in the expansion of the bulb have no appreciable effect on the results.

Since the expansion of a gas, especially hydrogen, is much more regular than that of either mercury or glass, and since the gas thermometer is but little affected by the irregularities of the expansion of its bulb, the gas rather than the mercury thermometer is to be regarded as the standard instrument, and determinations of temperature by the latter are to be corrected by adding the ascertained divergences between the two classes of instruments. These divergences are sometimes positive and sometimes negative in character. They are to be found in tabular form in the *Physikalisch-Chemische Tabellen* of Landolt and Boernstein.

Alcohol and Toluene Thermometers

Owing to its low freezing point alcohol has been much used in the preparation of thermometers for temperatures under the solidifying point of mercury. It is, however, an exceedingly defective material for the purpose. Its rate of expansion increases very rapidly with rising temperature and is greatly affected by the presence of small quantities of water. The amount of the alcohol which adheres to the wall of the thermometer tube increases with falling temperature to such an extent that, at different temperatures, very different quantities of the liquid are employed in the mere wetting of the glass. It is customary, in preparing these instruments, to fix the zero point in the usual way and to locate some second point by comparison with a standard thermometer. By means of these two fixed points the whole scale is then uniformly graduated.

When the alcohol and air thermometers are compared, large discrepancies are found. The divergence increases rapidly with falling temperature, and amounts to about 10° at -100° .

In some respects toluene is superior to alcohol as a material for low-temperature thermometers. It can be prepared in uniformly pure condition so that the instruments agree with one another, and its high boiling point (110°) makes it practicable to locate experimentally both of the usual fixed points of a thermometer, i.e. the freezing and boiling points of water. Nevertheless, the disagreement with the air thermometer at low temperatures is even greater in the case of the toluene than in that of the alcohol thermometer.

Determination of Temperatures by Means of Substances of Known Melting Points

It is often necessary in the laboratory, when the circumstances do not permit the use of a thermometer or a pyrometer, to ascertain within narrow limits the temperature which is

produced by a given heating arrangement, or to know that the highest temperature reached during an experiment lies between two limits. In such cases substances of known fusing points can generally be used with advantage. If it is found, for instance, that the temperature attained under the given conditions suffices for the fusion of sodium chloride but not for that of potassium carbonate, then it is known that the highest temperature reached is above 776° and below 835° . If the former fuses very readily while the latter shows no signs of having been in the least degree softened, it is reasonable to assume that the temperature was about 800° .

In this connection should be mentioned the so-called "Seeger cones." These are triangular truncated pyramids six centimeters in height which are made up of mixtures of silicates of gradually diminishing fusibility. They are much used in the baking of pottery and are often serviceable in the laboratory.

The following table gives the number and the melting point of each one of the series of Seeger cones.

022 = 590°	09 = 970°	4 = 1210°	16 = 1450°	28 = 1690°
021 = 620	08 = 990	5 = 1230	17 = 1470	29 = 1710
020 = 650	07 = 1010	6 = 1250	18 = 1490	30 = 1730
019 = 680	06 = 1030	7 = 1270	19 = 1510	31 = 1750
018 = 710	05 = 1050	8 = 1290	20 = 1530	32 = 1770
017 = 740	04 = 1070	9 = 1310	21 = 1550	33 = 1790
016 = 770	03 = 1090	10 = 1330	22 = 1570	34 = 1810
015 = 800	02 = 1110	11 = 1350	23 = 1590	35 = 1830
014 = 830	01 = 1130	12 = 1370	24 = 1610	36 = 1850
013 = 860	1 = 1150	13 = 1390	25 = 1630	37 = 1870
012 = 890	2 = 1170	14 = 1410	26 = 1650	38 = 1890
011 = 920	3 = 1190	15 = 1430	27 = 1670	39 = 1910
010 = 950				

Pyrometers

Of the many kinds of pyrometers which have been proposed or employed for the measurement of high temperatures, only two have any special interest for the chemist, — the *electric-resistance*

pyrometer and the *thermoelectric* pyrometer. The former is based on the fact that the electric resistance of metals varies with the temperature. Platinum is the metal employed in its construction. The best known instrument of this type is that of Callender. The thermoelectric pyrometer, on the other hand, utilizes the electro-motive force which is developed when a junction of two different metals or alloys is heated. The best known instrument of the second type is that of Le Chatelier. The metals employed in its construction are platinum and an alloy of platinum with ten per cent of rhodium. The electro-motive force which is developed when the junction of the two wires is heated is measured by means of a sensitive galvanometer.

CHAPTER III

THE CALIBRATION OF EUDIOMETERS AND THE MEASUREMENT OF GASES

EXERCISE VII

CALIBRATION OF A EUDIOMETER

I. PURIFICATION OF THE MERCURY

The apparatus represented in Fig. 7 is required. The large straight tube should have a length of not less than $1\frac{1}{2}$ meters and an internal diameter of 15–20 mm. The vertical distance between the two ends of the doubly bent small tube should be about one-tenth the length of the larger tube. The straight tube which is attached to the stem of the funnel is to be drawn down at the lower end to a minute orifice which will just permit the mercury, when under some pressure, to pass through it in a fine stream.

With the receiving vessel on the floor and the clamping stand on the table, fix the apparatus at the side of the table. Pour in more than enough mercury to fill the bent tube at the bottom, and then a dilute solution of ferric chloride (1 : 15 or 20) until the larger tube is nearly full. Remove from the receiver the mercury crowded out of the apparatus by the pressure of the liquid above, and pass the mercury to be cleansed through the funnel into the solution of ferric chloride. The operation is to be repeated until the metal is sufficiently pure for eudiometric purposes, i.e. until, after washing and drying, it shows no disposition to "tail out" when



FIG. 7

running along a clean glass surface. If the solution of ferric chloride becomes green in color, it must be replaced by a fresh one. If it is too concentrated, the mercury shows a disinclination to collect at the bottom in a sufficiently liquid form, and the apparatus, especially the small orifice at the lower end of the funnel, becomes clogged.

The frequently persistent refusal of finely divided mercury to coalesce is due to a coating of foreign matter which may be either solid or in solution, and the difficulty is to be overcome only by removing the covering which prevents contact between the minute globules. This may sometimes be accomplished by rubbing the material with a pestle or by warming and agitating it with water or hydrochloric acid. But the surest way of accomplishing the object is to force the mercury through finely woven cloth or a piece of chamois skin.

Replace the ferric chloride by water and wash the mercury thoroughly, renewing the water as often as may be thought necessary. Dry the mercury by wiping its surface with filter paper and by passing it through filters in which a large number of pin holes have been made.

Line a porcelain dish with several sheets of strong filter paper, place the mercury on the upper one, and dry still further at 105° in an air bath under a hood. The drying may be somewhat facilitated by placing glass rods or tubes between the paper and the porcelain dish in such a manner as to keep the two quite apart.

The advantage of this method of purification over those in which the mercury is simply agitated with the cleansing liquid lies in the very fine subdivision of the metal which is effected at the orifice of the funnel. The purification can take place only at the surface of contact between the two liquids; hence the desirability of increasing this surface to the greatest possible extent.

Solutions of other substances which readily attack the impurities, but act only slowly or not at all on the mercury, may be used in the place of the ferric chloride.

A supply of dry and sufficiently pure mercury may be maintained by keeping the metal, when not in use, under strong sulphuric acid to which mercurous sulphate has been added. The foreign metals, excepting silver, gold, and platinum, are converted into sulphates. The apparatus which serves as a reservoir must be of such construction that the mercury may be drawn off at the bottom and returned at the top. Ordinarily this apparatus consists of a glass globe with a tube and stopcock underneath and a neck for a stopper above. A large separating funnel may be used for the purpose. The neck is closed with a doubly perforated stopper through which are passed a funnel with a stopcock for the introduction of the mercury, and a calcium chloride tube to dry the air entering the apparatus.

Distillation in a vacuum — for which a variety of automatic stills have been devised — is also an excellent method for the purification of mercury.

Many of the metals when amalgamated oxidize very easily in contact with the air, giving rise to gray-colored films upon the surface of the mercury. The appearance of such films on mercury exposed to the air is, therefore, to be regarded as an evidence of impurity, while their absence is a sign of some value of the purity of the metal. The color of the films is due to the admixture of mercury in the metallic condition, and is not, as is often supposed, the result of the formation of gray sub-oxides of the metals attacked.

Advantage may be taken of the fact that some metals when dissolved in mercury are easily attacked by free oxygen, to purify mercury by means of the air. For this purpose currents of air are forced through the metal; or, better, the metal is allowed to fall through the air in fine streams,

II. CALIBRATION OF THE EUDIOMETER

Select a eudiometer with a millimeter graduation extending over not less than 70 centimeters. Compare the graduation, which is sometimes grossly incorrect, with that of some standard supposed to be reliable, e.g. with that of the barometer. Examine it with a magnifying glass for the minute cracks which are apt to appear where the platinum wires pass through the glass. Fill it with mercury, taking care to dislodge all air bubbles which become entangled between the mercury and the wall of the tube. This may be accomplished with the aid of a long whalebone, or by inclining the tube from time to time while filling and slowly returning it again to the vertical position. The lodging of air bubbles against the glass may be avoided altogether by filling very slowly and without interruption through a small glass tube which reaches to the bottom of the eudiometer. For this purpose it is necessary to have, placed above the eudiometer, a supply of mercury whose flow through the tube can be properly regulated.

Invert the filled eudiometer in a mercury trough having transparent sides. Fix it in a cork-lined clamp, using plumb lines suspended from the ceiling to determine when its position is vertical. If the length of the tube is greater than a barometric height, determine the length of the column in the eudiometer from the level of the mercury in the trough to the top of the meniscus; also the height of the barometer, using the telescope for both readings. After several hours repeat the readings. If the height of the barometer and that of the columns are unchanged, or if both have risen or fallen alike, the eudiometer does not leak. If, on the other hand, the tube is shorter than a barometric height, the existence of a leak will be detected by the accumulation of air in the top of the tube.

Eudiometers into which platinum wires have been fused for the explosion of gas mixtures are often ruined in consequence of the formation — especially at the time of an explosion — of

cracks in the glass around the wires. The fact that these cannot be detected by the eye, even when aided by a lens, is never a certain proof of the soundness of the tube. The cause of the difficulty is a slight inequality in the expansion coefficients of glass and platinum.

The calibrating cup, Fig. 8, is used for the introduction into the eudiometer of equal volumes of mercury. The capacity of the cup should not, in general, exceed 5 cc. Its edge is ground to a plane making a right angle with its axis. The covering glass is also ground on one side, while the other side is provided with a rubber ring — cemented to the glass — through which the thumb may be slipped. This arrangement enables the operator to manipulate the cup and its cover with one hand.

As a reservoir for the supply of mercury, a separating funnel, or even a burette, may be used. It is necessary only that the delivery tube of the vessel should be of small bore and of sufficient length below the stopcock to reach the bottom of the calibrating cup.

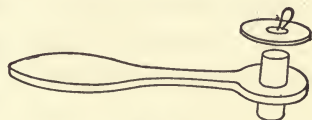


FIG. 8

Bring the cup under the reservoir so that the outlet of the latter rests upon the bottom of the former and slowly fill with mercury, lowering the cup as the filling progresses, but not enough to expose the end of the delivery tube until the cup is full. In this way the lodging of air bubbles between the mercury and the glass will be avoided. Bring the ground glass plate, which is carried on the thumb of the hand holding the cup, vertically down upon the surface of the mercury and gently rub it from side to side to remove superfluous metal. Pour the cupful through a funnel with a long stem of small bore into the eudiometer. It will probably be found that air bubbles have lodged between the glass and mercury, also that minute globules of the metal have attached themselves to the glass for a considerable distance up the tube. The former must be removed and the latter added to the main body of the mercury. Cover the hands with towels or mittens. Incline the eudiometer

with the closed end resting on the table and then revolve it to collect the scattered globules. Finally, bring the tube very slowly to the vertical position.

The detached globules may also be gathered up and the air bubbles released with the aid of a long piece of whalebone. In this way the danger of warming the tube by handling is avoided.

Fix the eudiometer in a vertical position with the aid of the plumb lines and read with the telescope the height of the mercury to the top of the meniscus. Continue the filling in of the mercury and the reading of the height of the column after each addition until the tube has been filled to a depth of not less than 400 mm.

It is obvious that the temperature of the mercury must remain very nearly constant during the whole of the time occupied in filling the eudiometer.

At some time during the calibration two cupfuls of mercury should be poured into weighing glasses and set aside for the purpose of determining the capacity of the calibrating cup. A record of the temperature of the mercury will also be required.

The use which is to be made of the readings obtained during the filling of the eudiometer will be illustrated by means of an example.

I	II	III	IV	V
21	596.4	28.4	$28.54 \times 21 = 599.34$	difference = + 2.94
20	568.0	28.9	" $\times 20 = 570.80$	" = + 2.80
19	539.1	28.9	" $\times 19 = 542.26$	" = + 3.25
18	510.2	29.0	" $\times 18 = 513.72$	" = + 3.52
17	481.2	29.1	" $\times 17 = 485.18$	" = + 3.98
16	452.1	29.1	" $\times 16 = 456.64$	" = + 4.54
15	423.0	29.1	" $\times 15 = 428.10$	" = + 5.10
14	393.9	29.1	" $\times 14 = 399.56$	" = + 5.66
13	364.8	29.3	" $\times 13 = 371.02$	" = + 6.22
12	335.5	29.2	" $\times 12 = 342.48$	" = + 6.98
11	306.3	28.8	" $\times 11 = 313.94$	" = + 7.64
10	277.5	28.4	" $\times 10 = 285.40$	" = + 7.90
9	249.1	28.3	" $\times 9 = 256.86$	" = + 7.76
8	220.8	28.5	" $\times 8 = 228.32$	" = + 7.52
7	192.3	28.0	" $\times 7 = 199.78$	" = + 7.48
6	164.3	27.9	" $\times 6 = 171.24$	" = + 6.94
5	136.4	27.9	" $\times 5 = 142.70$	" = + 6.30
4	108.5	27.7	" $\times 4 = 114.16$	" = + 5.66
3	80.8	27.8	" $\times 3 = 85.62$	" = + 4.82
2	53.0	27.5	" $\times 2 = 57.08$	" = + 4.08
1	25.5		" $\times 1 = 28.54$	" = + 3.04

In column I the cupfuls of mercury are numbered from 1 to 21 in the order in which they were poured into the tube. Column II gives the successive readings on the graduation of the eudiometer, and column III the difference between each reading and the one which precedes it, i.e. the number of millimeter divisions filled by the various cupfuls. It will be observed that the equal volumes of mercury fill quite different fractions of the tube's length, showing considerable irregularity in the caliber of the eudiometer. The first cupful fills a much smaller number of divisions than any one of the others, but this is owing to the fact that the graduation is not extended to the end of the tube.

If 25.5 (the first reading) is subtracted from 596.4 (the last), it is found that twenty cupfuls of mercury fill a space 570.9 mm. in length. The average length of tube filled by a cupful is

therefore $\frac{570.9}{20}$, or 28.54 mm. For this reason it was decided to regard the cup as containing 28.54 volume or calibration units. It is obvious that the capacity of the tube, from the closed end to the various points reached by the different cupfuls of mercury, can be found, in terms of the calibration unit, by multiplying 28.54 by the number of cupfuls which fill the tube to these points. This has been done for each cupful under IV. Column V contains the quantities which must be added to the actual readings in order to obtain their equivalents in calibration units. To obtain the value of other readings than those recorded in column II, a curve is employed. To construct this, the millimeter graduation on the tube is made the axis of abscissas, and the quantities to be added to the actual readings, i.e. those recorded under V, the ordinates. The curve is completed by drawing straight lines between the adjacent points thus established. It will be seen that in this case, as in the calibration of the thermometer by a similar method, only a limited number of points in the curve are established with certainty. The assumption that all other points in the curve lie in the straight lines joining these—in other words, that the change in the caliber of the tube is always uniform between two successive established points—is not any more correct in the case of a eudiometer than in that of a thermometer. In the calibration of a thermometer, as already shown, the number of correctly established points in the curve can be multiplied to any desired extent without diminishing the length of the thread. In the case of a eudiometer, on the contrary, the size of the cupful—the equivalent of the thread—must be diminished if a closer calibration is required.

The curve should be plotted upon cross-ruled paper with lines one millimeter or one-tenth of an inch apart, in such a manner that each space on the horizontal lines represents a millimeter division of the graduation on the tube, and each space on the vertical lines, one-tenth of a unit of the correction to

be made. It is advisable, in order to keep the curve of the corrections near the line representing the eudiometer, to indicate the addition of whole numbers, and to employ the curve only for the fractional parts.

The following is the usual, though less satisfactory, method of elaborating the calibration data. It will be seen that the second cupful of mercury which was poured into the tube occupied a space 27.5 mm. in length. If now 28.54—the number of calibration units in the cup—is divided by this number, there will be obtained, in terms of the calibration unit, the average value of a millimeter division between the first and second readings. The value of the millimeter spaces in all other parts of the tube may be obtained in the same way. The results of twenty such divisions are given under VI.

	VI	V.R.	COR. V.	V.R.	COR. V.
21	1.0049	26	29.06	46	49.81
20	0.9875	27	30.10	47	50.85
19	0.9875	28	31.13	48	51.89
18	0.9841	29	32.17	49	52.93
17	0.9808	30	33.21	50	53.97
16	0.9808	31	34.25	51	55.00
15	0.9808	32	35.29	52	56.04
14	0.9808	33	36.32	53	57.08
13	0.9741	34	37.36	54	58.11
12	0.9774	35	38.40	55	59.13
11	0.9910	36	39.44	56	60.16
10	1.0049	37	40.47	57	61.19
9	1.0085	38	41.51	58	62.21
8	1.0014	39	42.55	59	63.24
7	1.0193	40	43.59	60	64.27
6	1.0229	41	44.63	etc.	etc.
5	1.0229	42	45.66		
4	1.0303	43	46.70		
3	1.0266	44	47.74		
2	1.0378	45	48.78		

The volume capacity of the tube to 25.5, the first reading, is 28.54 calibration units, and if there is added to this 0.5189, — one half the value of the millimeter spaces in that part of the tube, — the corrected volume to the twenty-sixth division of the scale will be obtained, i.e. 29.06. The volume to the twenty-seventh, and the volumes to the succeeding divisions as far as the fifty-third, are found by adding the number 1.0378. From the fifty-third to the eighty-first division the number 1.0266 is to be added, etc. The usual form of tabulation is shown under V.R. and Cor. V., which signify volume read and correct volume respectively.

It will be found, on contrasting the two methods of dealing with the calibration data, that the first is less laborious and more correct than the second. It also presents the results in a form which is more convenient for use. The first assumes that any change in the caliber of the tube, within the space filled by a cupful of mercury, is gradual from reading to reading; while the second supposes the caliber of the tube to be uniform between two successive readings, i.e. that changes of caliber occur only where one cupful ends and another begins. The latter assumption is obviously more erroneous than the former. The corrections for the fractional parts of the readings must be found by calculation when the second method is employed, while the curve enables one to estimate them to the second decimal place by the eye.

It will be seen that neither method provides for the measurement of a gas volume smaller than the cup itself. If it is desired to find the volumes of smaller quantities of gas, a smaller calibrating cup must be used.

III. DETERMINATION OF THE VALUE OF THE MENISCUS

A correction for the meniscus is to be applied to any volume of gas measured over a liquid. If the liquid is mercury, the meniscus is convex and the correction is to be added; if it is

water or an aqueous solution, the meniscus is concave and the correction is to be subtracted.

Suppose, when the mercury is poured into the eudiometer for calibration purposes, that the first cupful gives a reading of 20 mm., as shown in Fig. 9. Then imagine the tube to be inverted and to contain enough gas collected over mercury to give the same reading, as shown in Fig. 10. It is evident, notwithstanding the fact that the readings are identical, that the volume of the gas in the second case is greater than that of the mercury in the first by the space *aa*; and that whenever



FIG. 9



FIG. 10

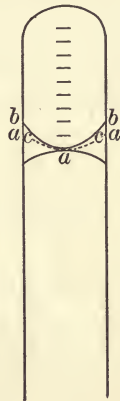


FIG. 11

any quantity of gas is measured, it will be necessary to add this space to its apparent volume in calibration units. This is known as the correction for the double meniscus, and the magnitude of the correction is now to be determined.

Fix the eudiometer in a vertical position and partially fill it with mercury. Read on the graduation of the tube, with the telescope, the highest point in the meniscus. Pour over the top of the mercury a few drops of a dilute solution of mercuric chloride. In a few moments the end of the mercury column will lose its convex form and become horizontal. Read again. The difference between the two readings is the correction for the

single meniscus, and twice this is the quantity always to be added to a gas volume measured in the tube.

The correction value of the meniscus varies with the diameter of the tube and the nature of the liquid. The following table gives the amount of the correction, as determined by Bunsen, for tubes of various diameters.

DIAMETER OF TUBE	WATER	7 PER CENT Na OH	MERCURY
14 mm.	1.10 mm.	0.70 mm.	0.57 mm.
15	1.03	0.63	0.53
16	0.97	0.57	0.48
17	0.91	0.51	0.44
18	0.87	0.47	0.38
19	0.84	0.44	0.32
20	0.82	0.42	0.26
21	0.80	0.40	0.20

IV. DETERMINATION OF THE VOLUME OF THE CALIBRATION UNIT

For most gas analytical purposes an arbitrary unit of volume, like the calibration unit, is sufficient; but it frequently happens that a knowledge of the volume of a gas in cubic centimeters is required. It is therefore desirable in every case to determine the value of the calibration unit in terms of the cubic centimeter. To do this, weigh the two cupfuls of mercury which were set aside while calibrating the tube, and correct half the sum of the two weights for displacement of air. The volume of the calibration unit will then be found by substituting the value of g , t , and V in the following equation:

$$c = g \frac{1 + 0.0001818 t}{13.5956 V}, \text{ in which}$$

c is the value to be found;

g is the weight of mercury;

0.0001818 is the mean expansion coefficient of mercury between 0° and 30° ;

t is the temperature of the mercury when measured off; 13.5956, the weight of one cubic centimeter of mercury at 0° ; and V , the number of calibration units in the cup.

Measurement of Gases over Water

We have now to consider under what restrictions a tube which has been calibrated with mercury may be used for the measurement of gases over water or other liquids than mercury. If a quantity of gas is introduced into a eudiometer filled with water, there are two conditions affecting its measurement which require attention: first, the water, in descending to make room for the gas, leaves a film upon the glass, thereby diminishing the capacity of the tube; second, the meniscus differs both in character and value from that of mercury.

There are various ways of ascertaining the amount of the correction to be made for the film, but as this error is small as compared with others which are encountered when gases are measured over any liquid except mercury, the correction is rarely attempted.

When a gas is collected over water in a tube which has been calibrated with mercury the correction for the meniscus is negative, and amounts to the difference between the water and the mercury meniscus. Suppose, Fig. 11, in calibrating a tube, that the first cupful had filled to the twentieth division on the graduation, and that afterwards a quantity of gas giving the same reading had been collected over water. The mercury meniscus is represented by the line aaa , and that of the water by bab . The volume of the mercury is known, it having been determined in the course of the calibration; but the volume of the gas over water is less than that of the mercury by the space cc , which is equal to the difference between a water and a mercury meniscus.

The Absorption of Gases by Liquids

It is often convenient and sometimes necessary to collect and measure gases over other liquids than mercury. But it should be borne in mind that the absorption and diffusion of gases are serious obstacles in the way of employing such liquids when the work in hand demands a high degree of accuracy; and one must consider in situations where convenience would be promoted by the use of another liquid than mercury whether or not the resulting unavoidable errors will be of tolerable magnitude. A brief recapitulation of some of the more important facts relating to the absorption of gases by liquids may be useful in this connection.

1. The absorption coefficient of a gas with respect to any particular liquid is the volume of the gas, measured under standard conditions of temperature and pressure, which a unit volume of the liquid will absorb when exposed in an atmosphere of the pure gas.

2. The Effect of Temperature. The power of liquids to retain gases decreases with rising temperature, hence changes in temperature are followed by changes in absorption coefficients; but the law which regulates the relation of absorption coefficients to temperature is not known.

3. The Effect of Pressure. The volume of a gas which a unit volume of a liquid will absorb is independent of the pressure. This is known as Henry's Law. But, since the amount of matter in a given volume of gas is proportional to the pressure, the absorption coefficients are, according to the definition, also proportional to the pressure. It will be seen that the term absorption coefficient is fully defined only when accompanied by a statement of both temperature and pressure.

4. Absorption from a Mixture of Gases. From a mixture of gases each constituent will be absorbed according to its partial pressure, i.e. according to the proportion of the total pressure which is due to its presence. Stated in another way, each constituent will be absorbed to the same extent that it would be

if, without changing the volume, all the other components of the mixture were removed. This is known as Dalton's Law of Partial Pressures. Its application to specific cases will be made clearer by an illustration. At 0° and under a pressure equal to 760 mm. of mercury the absorption coefficients of nitrogen and oxygen are 0.02035 and 0.04114 respectively; that is, under the given conditions, a liter of water would absorb 20.35 cc. of gas in an atmosphere of pure nitrogen and 41.14 cc. in an atmosphere of pure oxygen. But suppose the liter of water is exposed under the same conditions of temperature and pressure to the air, which is a mixture of four volumes of nitrogen with one of oxygen. According to the law of partial pressures the water will absorb $\frac{4}{5}$ of 0.02035 of nitrogen and $\frac{1}{5}$ of 0.04114 of oxygen; that is, after saturation, it will be found to contain 16.28 cc. of nitrogen and 8.23 cc. of oxygen.

The embarrassing effects of absorption phenomena upon gas analytical operations when other liquids than mercury are used are quite obvious; nevertheless it may not be superfluous to call attention to a few of them.

Suppose a mixture of gases is required, for any purpose, to pass through a liquid. The liquid will become saturated with the various constituents of the mixture in accordance with the absorption coefficient of each and the law of partial pressures. The consequence is that for a time the gas which passes out of the liquid will differ in composition from that which entered. The alteration in the composition of the gas will cease, of course, when the liquid has become fully saturated. For the same reason, a mixture of gases standing over a liquid will suffer a change in composition unless the liquid is previously saturated with a mixture of identical composition. The practice of first saturating a liquid with the same kind of gas that is afterwards to be passed through it, or collected over it, is very common in gas analysis but is not without its disadvantages. A simple example will illustrate this. Suppose a gas containing a , b , and c has been collected over water previously saturated

with some of the same kind of gas, and is to be analyzed by removing the various constituents in turn by means of appropriate absorbents and measuring the contraction which takes place after each withdrawal. If other gases, e.g. air, are kept out of the water, and changes of temperature do not bring about a change in the relative magnitudes of the absorption coefficients of the different components, the gas would maintain its composition indefinitely. But suppose one of the constituents, e.g. a , is removed. The water will then be supersaturated as far as a is concerned, and probably undersaturated as regards b and c ; consequently a small portion of b and c will enter the water while the residue becomes contaminated with a .

Another difficulty which is encountered when other liquids than mercury are employed for the isolation of gases is the fact that two gases cannot be permanently separated by a liquid which is capable of gas absorption. The usual source of trouble in this connection is the air. Suppose, by way of illustration, that a body of hydrogen is standing in a eudiometer over water which, as usual, is also in contact with air. From the one side the water will saturate itself with hydrogen, and from the other with the oxygen and nitrogen of the air; and the law of partial pressures will require the hydrogen to pass out of the water into the atmosphere, while the constituents of the air, for the same reason, enter the space occupied by the hydrogen. Theoretically this exchange would continue until the two gases became identical in composition; but since the volume of the air is infinitely greater than that of the hydrogen, the final result would be a complete replacement of the latter by the former.

The facts cited above will suffice, it is hoped, to impress upon the student the need of great circumspection in dealing with gases. In this field, as in all other kinds of quantitative work, when a given course of procedure suggests itself or is recommended, one should first of all, and as a matter of habit, scrutinize the *sources of error* and consider the means by which they may be avoided or minimized.

*The Correction of Gas Volumes for Pressure, Temperature,
and Water Vapor*

The space which any given mass of gas will occupy depends on the pressure to which it is subjected, its temperature, and the amount of water vapor which it contains. Hence, for the purpose of comparing gases with respect to mass, it is necessary to reduce the observed volumes to those which the gases would have if measured under the same conditions.

I. The Correction for Pressure

When a given mass of gas is measured under different pressures, without change of temperature, its various volumes are found to be inversely proportional to the pressures. That is, if the pressure is doubled, the volume will be halved; or if the pressure is halved, the volume will be doubled, etc. Stated in another way, the product of the pressure and the volume is a constant. This relation of the volume of a gas to the pressure upon it is known as Boyle's law — also as the law of Mariotte. Gases which cannot be condensed to liquids except at very low temperatures — like hydrogen, oxygen, nitrogen, carbon monoxide, and methane — obey the law within ordinary ranges of pressure but deviate from it more or less under high pressures. Gases easily condensed to liquids, likewise the vapors of liquids, do not conform to the law until heated considerably above their temperatures of liquefaction.

If a gas is confined over a column of liquid which is, in turn, in free communication with the air, the pressure of the gas and that of the column of liquid are together equal to the pressure of the air. Hence, in order to find the pressure of the gas, we must subtract the pressure of the column of liquid from the height of the barometer. If the liquid employed to isolate the gas is mercury, the difference between its height, corrected to 0°, and that of the barometer, also corrected, is the value

required. But when another liquid is used the length of an equivalent column of mercury must first be found. To do this, the height of the column is multiplied by the specific gravity of the liquid and the product divided by 13.596, the density of mercury at 0°. If the liquid is water, the specific gravity corresponding to its temperature will be found in any collection of chemical tables; otherwise it will probably have to be determined.

The commonly accepted standard for pressure is that which at 0° will support a column of mercury 760 mm. in height, and all gases measured under other pressures are corrected to the volumes which they would have under this. The formula for the correction is

$$V_1 = V \frac{h}{760}, \text{ in which}$$

V_1 is the volume under standard pressure,

V the observed volume, and

h the pressure — with all necessary corrections applied — under which the gas was measured.

Ordinarily h is simply the difference between the height of the barometer and that of the mercury column over which the gas was measured — both corrected for temperature; but in more refined work, such as the determination of atomic weights and the densities of gases, a correction for latitude and altitude is also to be made. This is to be applied, of course, not to the barometer and the column separately, but only to the difference between them, i.e. to h .

II. The Correction for Temperature

If the temperature of a gas is raised, without change of pressure, from 0° to 100°, its initial and final volumes are related to each other as 1 to 1.367. For each increase in temperature of one degree, the expansion amounts to 0.00367, $\frac{1}{273}$ of its volume

at 0° . This law was discovered simultaneously by Gay-Lussac and Dalton.

The standard temperature for the measurement of gases is 0° , and the formula for finding what volume any gas, measured at a higher temperature, would have at the standard temperature is

$$\frac{V}{1 + 0.00367t}, \text{ in which}$$

V is the observed volume,

t the temperature of the gas at the time of measurement, and 0.00367 the expansion coefficient of gases.

If the temperature at the time of measurement is below 0° , the formula becomes

$$\frac{V}{1 - 0.00367t}.$$

The formula for finding the volume of gases under standard conditions, both of temperature and pressure, is

$$\frac{V}{1 + 0.00367t} \times \frac{h}{760}.$$

III. The Correction for Water Vapor

Gases are measured either dry or fully saturated with water vapor — usually in the latter condition. The correction of the volume of a saturated gas for the water vapor which it contains is effected by subtracting the known tension or pressure of the vapor — expressed in millimeters of mercury — from h , the pressure under which the gas was measured.

The complete formula for the reduction of observed gas volumes to standard conditions of temperature, pressure, and dryness is

$$\frac{V}{1 + 0.00367t} \times \frac{h - \text{tension of water vapor}}{760}.$$

A gas standing over water for any length of time necessarily becomes saturated with vapor. The same is true of a gas which

is passed through water, but it is to be remembered with reference to the latter method of effecting saturation that if the temperature of the gas should afterwards rise, more water will be required. When a gas is collected over mercury, the water necessary for its saturation may be provided by moistening the inner wall of the containing vessel before filling with mercury, or by introducing afterwards a small drop of water.

It is also to be remembered that the tension of water vapor over an aqueous solution is, at a given temperature, always less than over pure water. It is therefore necessary as a rule, since the vapor tension of but few solutions is known, finally to measure a gas over water or mercury, or in the dry condition over a liquid which, like concentrated sulphuric acid, has practically no vapor tension of any kind.

The student should practice the reduction of gas volumes, applying all possible corrections, until he is thoroughly familiar with the principles on which these corrections are based, and until he has acquired some facility in computations of this kind. Afterwards tables which have been prepared to lighten the labor of such calculations may be resorted to. All required tables will be found in the collection of Landolt and Boernstein. Those most frequently used in connection with gasometric work are:

Corrections of the barometer for temperature, for latitude, and for altitude.

Corrections for meniscus in tubes of different diameters.

Reduction of water pressure to mercury pressure.

Values of $\frac{h}{760}$.

Values of $1 + 0.00367 t$.

Tension of aqueous vapor over water and certain solutions.

The weights of unit volumes of gases.

Absorption coefficients of gases in liquids.

*The Passage of Gases through Rubber **

It is important for the student to know that rubber, which in the form of tubing is constantly used in the laboratory to connect the different parts of apparatus and to direct the flow of gases, is permeable to gases—including water vapor—and to some of them to a high degree. The passage of gases through rubber does not obey the law of diffusion which requires that the rates of diffusion shall be inversely proportional to the square roots of the densities of the gases. This will appear from the following table which gives the relative volumes of some of the commoner gases which will pass through a rubber septum in a unit of time.

GAS	RATE OF DIFFUSION	SQUARE ROOT OF DENSITY
Nitrogen	1.000	3.7416
Carbonic oxide	1.113	3.7416
Atmospheric air	1.149	3.7947
Marsh gas	2.148	2.8284
Oxygen	2.556	4.0000
Hydrogen	5.500	1.0000
Carbon dioxide	13.585	4.5825

According to the law of gaseous diffusion, carbon dioxide should pass through a septum only 0.22 as rapidly as hydrogen, while its actual rate of passage through rubber is 13.585 times as rapid as that of nitrogen and 2.47 times as rapid as that of hydrogen. In other words, carbon dioxide penetrates rubber 16.6 times too rapidly when compared with nitrogen and 11.23 times too rapidly when compared with hydrogen. Sulphur dioxide exhibits this power of penetrating rubber to an even more remarkable degree than carbonic anhydride. The disagreeable odor of rubber tubes through which illuminating gas is passing and the well-known fact that the gas in passing

* The student should read Thomas Graham, "On the Absorption and Dyalytic Separation of Gases by Colloid Septa," *Philosophical Transactions*, 1866, p. 399; or *Researches of Thomas Graham*, p. 235.

through such tubes suffers a notable loss in illuminating power are familiar proofs of the readiness with which rubber is penetrated by gases.

Equality of gaseous pressure upon the two sides does not prevent the passage of gases through an intervening wall of rubber; hence gases conducted through rubber tubing or in contact with rubber connections or stoppers must, in general, suffer some change in composition. The important practical rule to be deduced from the foregoing statements is that, in dealing with gases, rubber connections and rubber stoppers are to be avoided wherever it is practicable to dispense with them. If the parts of an apparatus must be connected by means of rubber, the ends to be joined should be accurately fitted to each other and brought close together in the connection. Again, if a gas is to be transported for a considerable distance, glass tubes,



FIG. 12

with a minimum of rubber connections, should be employed. The common practice of using long stretches of rubber tubing for this purpose is a sure evidence either of ignorance or of a certain lack of aptitude for good experimental work.

Figures 12 and 13 exhibit arrangements which may often be used with advantage to prevent diffusion of gases through rubber connections. The outer or "jacket" tubes are filled with mercury. Such protection, however, does not wholly remove the objection to the use of rubber connections, since rubber is capable of absorbing and retaining considerable volumes of certain gases. This is especially true of oxygen, carbon dioxide, sulphur dioxide, and some of the hydrocarbons.



FIG. 13

Rubber connecting tubes should usually be tied, especially when the gaseous pressure upon the inner and outer walls is unequal. The best material for such ligatures is waxed shoemaker's thread — so-called "waxed end."

CHAPTER IV

CALIBRATION AND GRADUATION OF APPARATUS FOR THE MEASUREMENT OF LIQUIDS

EXERCISE VIII

I. DETERMINATION OF THE CAPACITY OF A MEASURING FLASK BY WEIGHING WATER

If a large and sufficiently accurate balance is at the disposal of the student, a liter flask should be employed in this exercise, otherwise a smaller one may be selected.

Place near the balance, several hours before it is required for use, a sufficient quantity of distilled water. The containing vessel should be closed, since the temperature of evaporating water is usually somewhat below that of the surrounding atmosphere.

Put upon the left-hand pan of the balance a weight—a beaker containing shot will suffice—which is heavier than both the flask and the water to be weighed. Suspend the closed flask from the right-hand stirrup by means of a platinum wire and add weights to the pan underneath until equilibrium is obtained, or until the deficit or excess of weight can be deduced from the sensibility of the balance.

Take the temperature of the water and that of the air in the vicinity. If both are the same, fill the flask nearly to the mark on the neck through a funnel with a long stem, or one whose stem has been extended by attaching to it a small glass tube, taking care not to wet the glass above the mark. Remove the funnel and continue the filling with a glass tube—one end of which is drawn out to a fine point—until the bottom of the

meniscus is on a level with the mark. If, in spite of precautions, the neck above the mark has been wet, the water must be removed. This is best done by means of a strip of filter paper rolled into the form of a small cylinder.

Place the filled flask (closed) on the pan and add weights to equilibrium. The difference between the weights added when the flask was empty and afterwards when it was filled is the apparent weight of the water, i.e. its weight without correction for air displacement. Find its weight in a vacuum.

Divide the corrected weight of the water by its density. This will give its volume in cubic centimeters and the capacity of the flask at the temperature at the time of weighing. Find the capacity of the flask at 4°, 15°, 17.5°, and 20°, using 0.000025 as the cubical expansion coefficient of glass. The following table gives the density of water — the weight of one cubic centimeter and the volume of one gram of water (corrected weight) — between 0° and 25°.

Density and Volume of Water between 0° and 25°

TEMPER- ATURE	DENSITY	VOLUME cc.	TEMPER- ATURE	DENSITY	VOLUME cc.
0°	0.999878	1.000122	13°	0.999430	1.000570
1	0.999933	1.000067	14	0.999297	1.000703
2	0.999972	1.000028	15	0.999154	1.000847
3	0.999993	1.000007	16	0.999004	1.000997
4	1.000000	1.000000	17	0.998839	1.001162
5	0.999992	1.000008	18	0.998663	1.001339
6	0.999969	1.000031	19	0.998475	1.001527
7	0.999933	1.000067	20	0.998272	1.001731
8	0.999882	1.000118	21	0.998065	1.001939
9	0.999819	1.000181	22	0.997849	1.002156
10	0.999739	1.000261	23	0.997623	1.002389
11	0.999650	1.000350	24	0.997386	1.002621
12	0.999544	1.000456	25	0.997140	1.002868

II. THE GRADUATION OF A MEASURING FLASK

Warm one side of a piece of paraffin or beeswax and with it rub the neck of the flask to be graduated; then warm the neck over a flame and turn the flask until the molten wax distributes itself uniformly over the glass in a film thin enough to be moderately translucent when cold.

The second step is to ascertain how much water of the temperature of the balance room must be weighed into the flask in order that the flask may have the desired capacity, below the mark, at some standard temperature which, of course, should be the prevailing temperature of the laboratory. We will suppose that the temperature of the balance room and of the water is 18° , while the flask is to be graduated to hold a liter at 20° , the latter being the usual temperature of the laboratory. If the capacity of a flask at 20° is 1000 cc., its capacity at any lower

temperature will be $\frac{1000}{1 + 0.000025 t}$. At 18° it will be $\frac{1000}{1.000050}$, or 999.95 cc. The volume of a gram of water at 18° (see table) is 1.001339 cc.; the weight of water to be introduced into the flask is, therefore, $\frac{999.95}{1.001339}$, or 998.613 grams. This, however,

is weight in a vacuum. To find the weight of the water in the air, we must deduct the weight of 999.95 cc. of air, less the weight of the air displaced by the brass weights. The volume of the weights is $\frac{998.613}{8.4}$, or 118.88 cc.; and the volume of the

air whose weight is to be deducted is $999.95 - 118.88$, or 881.07 cc. The average weight of a cubic centimeter of air is 1.2 milligrams; 881.07×0.0012 , or 1.057 grams, is therefore the weight to be deducted. That is, in order that the flask may have a capacity of one liter at 20° , there must be weighed into it at 18° $998.613 - 1.057$, or 997.556 grams of water.

The general formula for finding the weight in the air of an object whose weight in a vacuum is known is

$$\frac{W}{1 + \left(\frac{1}{\bar{d}} - \frac{1}{d_1} \right) 0.0012}, \text{ in which}$$

W is the weight in a vacuum,

$\bar{d}$ the density of the object, and

d_1 the density of the weights.

Having ascertained the weight of water required and having weighed the flask, fill in through a funnel having a long stem until the water reaches the neck and then weigh. Calculate approximately what volume of water remains to be introduced and add very nearly the required amount from a graduated pipette. Weigh again, remove weights equal to the weight of the water still to be introduced, and then add water from a small glass tube with a fine delivering end until equilibrium is obtained. In view of the volume of water required to make an appreciable change in the level of the meniscus, it is probably useless, in graduating a measuring flask, to attempt to weigh the water accurately to within less than 10 milligrams, since this weight of water would have a volume of only about 0.01 cc.

With a sharp-pointed piece of steel, e.g. a round file ground to a sharp point, scratch a number of short horizontal lines in the wax on a level with the bottom of the water meniscus. Continue the line entirely around the neck and etch it into the glass with hydrofluoric acid. In some laboratories there is in use a simple adjustable arrangement which holds the steel point in the proper position against the paraffined neck while the flask is revolved. Lines cut in this way are usually more satisfactory than those produced in the manner described above.

III. THE CALIBRATION OF BURETTES BY MEANS OF MERCURY

A burette may be calibrated with mercury in much the same manner as a eudiometer; but, since these instruments are used mainly for the measurement of liquids which leave a film upon the glass, and hence deliver less than their full capacity, the volume of the film must be determined and applied as a correction to the results obtained by the mercury. The method is sufficiently accurate, but so cumbersome that it is not often resorted to. The exercise may therefore be omitted. Nevertheless the student should construct for himself a complete working plan for such a calibration.

The System of Mohr

Owing to the somewhat laborious corrections which are rendered necessary by a strict adherence to the liter as the unit of volume, Mohr proposed to regard as the standard for liquid-volumetric work the space occupied by a kilogram of water when the same is weighed in the air with brass weights at a temperature of 17.5° . The advantages claimed by the author for his system are:

1. The correctness of graduated apparatus is easily tested.
2. The measuring apparatus can be used without correction—at a temperature easily secured and maintained—for the determination of the specific gravities of liquids.

The system of Mohr obtained a wide currency in several countries, though modified here and there by the substitution of other temperatures, e.g. 15° for the standard 17.5° of its author. Of late, however, the system has rapidly lost ground and it is doubtless destined to disappear altogether in the near future.

The following table gives for several temperatures the corrected weight and the volume of the water which in the air will balance a thousand grams of brass of specific gravity 8.4, i.e. a kilogram brass weight.

TEMPERATURE	CORRECT WEIGHT	VOLUME
0°	1001.0573 gr.	1001.1851 cc.
4	1001.0511	1001.0571
10	1001.0575	1001.3218
12.5	1001.0578	1001.5811
15	1001.0582	1001.9168
17.5	1001.0587	1002.3301
20	1001.0592	1002.8122
22.5	1001.0599	1003.3626
25	1001.0606	1003.9742
27.5	1001.0614	1004.6505
30	1001.0623	1005.3804

It will be seen that the strictest adherence to a fixed temperature is necessary in order that a volume unit like that proposed by Mohr may have real value as a working standard. But the temperature recommended by the author of the system, 17.5°, has not been adhered to in the graduation of apparatus; neither has any other particular standard temperature been adopted by common consent. This divergence — due apparently to the lack of uniformity among the different laboratories in respect to what may be called prevailing temperature — has resulted in much confusion and, consequently, in a lack of precision in volumetric work. More unfortunate still has been the confusion of mind and the errors in practice due to the custom of calling the Mohr volume unit a *liter* and its submultiples *cubic centimeters*. It may be asserted with considerable confidence that the introduction of the Mohr system is largely responsible for the widespread impression that the volumetric system of analysis is necessarily less accurate than the gravimetric, and that it is therefore suited only to work of a rough kind. A sufficient explanation of the origin of this mistaken judgment appears when one finds in use side by side and uncalibrated, as he often may, apparatus which has been graduated according to the Mohr system for 17.5° and for 15°, and also according to the true liter.

EXERCISE IX

THE CALIBRATION AND GRADUATION OF MEASURING FLASKS AND THE CALIBRATION OF BURETTES

With the aid of the apparatus which is explained below, the student should calibrate—and regraduate if they are found to be incorrect—the following flasks: 1 l., $\frac{1}{2}$ l., and $\frac{1}{4}$ l. He should also calibrate not less than three burettes.

The apparatus represented in Fig. 14 is employed both for the graduation and the calibration of half-liter and liter measuring flasks. The delivering capacity of the bulb between the mark on the upper stem and the zero mark on the lower one must not exceed 500 cc. at the highest temperature at which the instrument is to be used; while the combined delivering capacity of the bulb and the graduated portion of the lower stem must not be less than half a liter at 0°. The lower stem

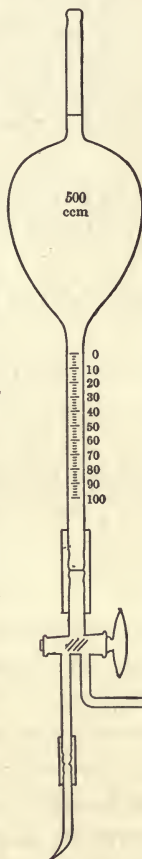


FIG. 14

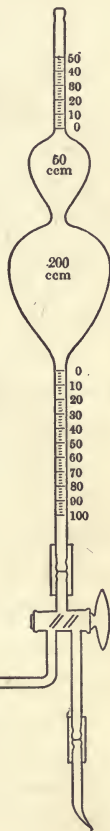


FIG. 15

is graduated in millimeter divisions which are numbered in both directions in order that the instrument may be used in the inverted position if desired.

For the purpose of explaining the method of preparing an instrument of this kind for use, an account of an actual calibration will be given. The water delivered by the bulb and also that delivered by the graduated portion of the lower stem was weighed and its temperature noted. The delivering capacity of the bulb and of the stem was then calculated by the formula

$$V = P \frac{p}{d}, \text{ in which}$$

P is the weight of the water when weighed in the air with brass weights (497.769 grams for the bulb and 3.0708 grams for the stem),

p is the weight in a vacuum of one gram of water weighed in the air with brass weights (1.001059 grams at ordinary temperatures), and

d is the density of the water at the temperature of weighing (21.4°).

In this way the delivering capacity of the bulb at 21.4° was found to be 499.324 cc., and that of the stem at the same temperature 3.081 cc.

The delivering capacity of the bulb at 0°, 4°, 10°, 12.5°, 15°, 17.5°, 20°, 22.5°, 25°, 27.5°, and 30° was calculated by the formula

$$V_t = V(1 + \gamma(t - t_0)), \text{ in which}$$

γ is the cubical expansion coefficient of glass (0.000025), t , is the temperature 0°, 4°, or 10°, etc., and t_0 is the temperature of the water at the time of weighing.

The results of these calculations are given in the second column of the table which follows. No corresponding calculation was made for the stem because the change in its capacity between 0° and 30° amounts to less than 0.0025 cc. The inequalities of its bore were also found to be insignificant. Each millimeter division of the stem was therefore regarded as having a delivering capacity of 0.03081 cc. at all temperatures between 0° and 30°.

The instrument was then ready for finding the capacity of any graduated half-liter or liter flask at any of the temperatures mentioned above. For this purpose a small glass tube drawn out and curved at one end, and long enough to reach the mark on the neck of the measuring flask, is attached to the delivering tube of the three-way stopcock, while the other tube of the stopcock is connected with a supply of water situated somewhat higher than the pipette. Water is allowed to flow in and fill the whole apparatus—including the delivery tube below the stopcock—to the mark on the upper stem. The flask whose capacity it is desired to find is filled to the mark from the pipette. If the quantity delivered from the stem is added to any number in the second column of the table, we shall obtain the capacity of the flask at the corresponding temperature in the first column. This is true of a half-liter flask; in the case of a liter flask the pipette must be twice filled, and the volume delivered by the stem is, of course, to be added to twice the numbers in the second column.

Since the pipette and the flask are of the same material, and therefore expand and contract alike for equal changes of temperature, the temperature of the water at the time of the experiment need not be known.

The next step was to find to what points on the graduated stem the water must be drawn in order to graduate a half-liter flask for each of the temperatures included in the first column. This was done by dividing the difference between 500 and the several numbers in the second column by 0.03081, the delivering capacity of one division of the stem. The results are given in the third column. To graduate a half-liter flask for any of the temperatures in the first column, it is necessary only to empty into it the bulb and then the corresponding number of stem divisions indicated in the third column. If it is desired to have the flask correct at 0° , 30.9 stem divisions will be added; at 4° , 29.3 divisions, etc. Here again the result is correct whatever may be the temperature of the water at the

time of the experiment. To graduate a liter flask, the bulb twice full and twice the indicated number of stem divisions must be added.

To prepare the instrument for use in the graduation and verification of apparatus when the so-called Mohr system is to be employed (i.e. when the correction for air displacement is to be dispensed with), the quantities in the second column were divided by the volumes at the different temperatures of one gram of water when weighed in the air with brass weights. These are :

TEMPERATURE	VOLUME	TEMPERATURE	VOLUME
At 0°	1.001185 cc.	At 20°	1.002812 cc.
4	1.001057	22.5	1.003363
10	1.001322	25	1.003974
12.5	1.001581	27.5	1.004651
15	1.001917	30	1.005380
17.5	1.002330		

The results are recorded in the fourth column of the table. The final step was to find to what point on the stem the water must be drawn in order to graduate a half-liter flask on the Mohr system for each of the temperatures recorded in the first column. For this purpose the capacity of the stem (3.081 cc.) was divided by 1.00233, the true volume of the Mohr unit at 17.5°, which gave 3.0738 as the capacity of the stem in Mohr units, or 0.030738 as the capacity of a single division. The differences between 500 and the several numbers in the fourth column were then divided by 0.030738, giving the numbers which are recorded in the fifth column. Strictly, each difference should be divided by a different number, but the maximum error which could ever result from regarding the volume of a gram of air-weighed water as constant between 0° and 30° is in this instance less than 0.01 cc. and therefore inappreciable.

TEMPERATURE	CAPACITY OF BULB IN CC.	DIVISIONS OF STEM TO BE ADDED	CAPACITY OF BULB IN MOHR UNITS	DIVISIONS OF STEM TO BE ADDED
0°	499.048	30.9	498.457	50.2
4	499.098	29.3	498.571	46.5
10	499.176	26.7	498.517	48.2
12.5	499.208	25.7	498.420	51.4
15	499.241	24.6	498.286	56.1
17.5	499.273	23.6	498.112	61.4
20	499.304	22.6	497.937	67.1
22.5	499.338	21.5	497.664	76.0
25	499.372	20.4	497.395	84.7
27.5	499.403	19.4	497.091	94.6
30	499.436	18.3	497.763	105.3

Capacity of one stem division in cc. = 0.03081.

Capacity of one stem division in Mohr units = 0.030738.

The apparatus represented in Fig. 15 is used for the calibration and graduation of smaller flasks. The capacities of the bulbs and of the graduated stems are subject to the same limitations as in the preceding case; that is, the delivering capacity of the smaller bulb must not exceed 50 cc. and that of the larger one 200 cc. at the highest temperature at which the instrument is to be used, while the combined capacity of each bulb and its graduated stem must not be less than 50 cc. and 200 cc. respectively at 0°. The delivering capacity of each bulb and stem at different temperatures is determined and the results are tabulated in the manner previously explained. 50-cc., 200-cc., and 250-cc. flasks can be graduated or their capacities determined by a single filling of the pipette. To graduate or calibrate a 100-cc. flask, the smaller bulb must be twice filled. The stop-cock may, of course, be attached to either end of the instrument.

The apparatus represented in Fig. 16 is for the calibration of burettes. The graduation upon the stem is in millimeters. The largest bulb has a delivering capacity of somewhat less than

50 cc. and, together with the graduated stem above, is employed to determine the total delivering capacity of a burette at any temperature. The limitations in respect to capacity are here

the same as in the case of the pipettes previously described; that is, the bulb must deliver less than 50 cc. at 30° , while the bulb and stem together must deliver not less than 50 cc. at 0° . The delivering capacity of the stem and the bulb at different temperatures is determined in the same way as in the case of the pipettes, and the results are tabulated in the same form.

The smaller bulbs are employed to determine the inequalities of caliber in a burette. The smaller one delivers less than 2 cc. at 30° , while the bulb and the graduated portion of the stem underneath together deliver not less than 2 cc. at 0° . The larger of the two bulbs and the graduated portion of the stem above it are subject to similar limitations. As will appear when the method of using the apparatus is explained, the capacity of the small bulbs need not be determined by weighing the water which they deliver.

Between the pipette and the burette a T tube is inserted whose third limb is connected with a supply of water situated above the upper limit of the

graduation on the burette. By means of this arrangement the burette and the pipette may be filled independently.

The procedure in calibrating a burette is as follows: The burette and the pipette are both filled with water to the upper

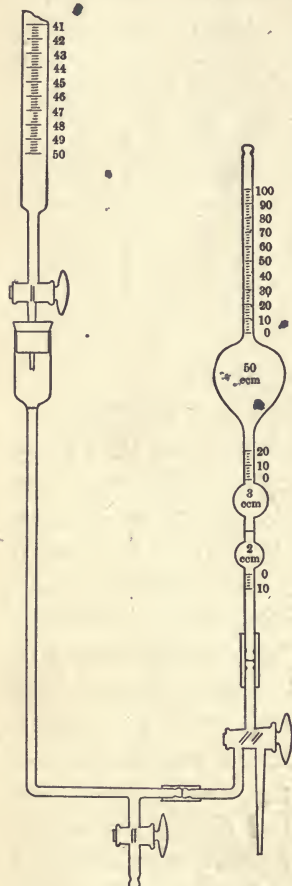


FIG. 16

limits of their graduation. The pipette is then emptied to the beginning of the graduation under the large bulb. Next, the water in the burette is allowed to flow into the pipette until the whole of the graduated portion is emptied. The water rises into the stem of the pipette, and the total delivering capacity of the burette at any temperature may be found by adding to the known delivering capacity of the bulb at that temperature the volume of the water in the stem.

Having found its total capacity, the burette is again filled, and the water in the pipette is drawn down to the zero mark under the smallest bulb. The bulb is then filled from the burette and the reading on the burette recorded. The bulb is emptied, refilled, and a second reading recorded. This series of operations is repeated until less than a bulbful of water remains in the graduated portion of the burette. The next step is to find the volume of the water drawn off in the manner described, and through this the delivering capacity of the bulb. How this is to be accomplished will be explained by means of the following example of a calibration.

A burette which had been graduated according to the Mohr system for 15° , but which was to be used for solutions prepared for 20° ,—that being the prevailing temperature of the laboratory,—was found to have at 20° a delivering capacity of 50.258 cc. The burette was filled and the water drawn off in quantities which exactly filled the smallest bulb of the pipette. The readings upon the burette corresponding to the successive bulbfuls are given in the table under *R*. The twenty-fifth and last reading was 49.52. The capacity of the burette to this point on its graduation was found, by the proportion

$$50 : 50.258 :: 49.52 : x, \text{ to be } 49.7755 \text{ cc.}$$

The capacity of the bulb used in the calibration was, therefore, $\frac{49.7755}{25}$, or 1.99102 cc. The true volumes corresponding to the readings were then found by multiplying 1.99102 by the series of numbers from 1 to 25. The results are given in the table

under *C.R.* The differences between the corresponding numbers under *R.* and *C.R.*, i.e. the quantities to be added as corrections to the actual readings, are given under *D.* Finally, a curve of corrections for the burette was plotted upon cross-ruled paper, using a line representing the graduation upon the burette as the axis of abscissas and the corrections under *D* as ordinates.

	R.	C.R.	D.		R.	C.R.	D.
1	1.95	1.99	+ 0.03	14	27.70	27.87	+ 0.17
2	3.94	3.98	+ 0.04	15	29.70	29.87	+ 0.17
3	5.93	5.97	+ 0.04	16	31.68	31.86	+ 0.18
4	7.94	7.96	+ 0.02	17	33.65	33.85	+ 0.20
5	9.91	9.96	+ 0.05	18	35.62	35.84	+ 0.22
6	11.90	11.95	+ 0.05	19	37.60	37.83	+ 0.23
7	13.85	13.94	+ 0.09	20	39.59	39.82	+ 0.23
8	15.84	15.93	+ 0.09	21	41.58	41.81	+ 0.23
9	17.83	17.92	+ 0.09	22	43.56	43.80	+ 0.24
10	19.78	19.91	+ 0.13	23	45.55	45.79	+ 0.24
11	21.74	21.90	+ 0.16	24	47.54	47.78	+ 0.24
12	23.75	23.89	+ 0.14	25	49.52	49.78	+ 0.26
13	25.74	25.88	+ 0.14		50.00	50.26	+ 0.26

The system of graduation and calibration of volumetric apparatus here described is equally applicable to all varieties of graduation — whether according to the Mohr or the metric unit, or in millimeters — and also to all temperatures. With its aid volumetric apparatus of the most miscellaneous character, as regards system and accuracy of graduation, can be brought into harmony and used side by side.

All of the required apparatus — excepting, of course, the three-way stopcock — can be made in the laboratory from ordinary full-pipettes and without the aid of expert workers in glass. How simply this may be done in the case of the instruments for the graduation and calibration of measuring flasks will appear from the appended directions for the conversion of a 100-cc. pipette.

Select a 100-cc. full-pipette having the mark on the upper stem near the bulb. Substitute it — delivery end up — for the calibrating pipette in the arrangement represented in Fig. 16. Fill the burette and pipette with water and then empty the latter to the mark on the stem nearest the stopcock. Fill into the pipette from the burette about 99.5 cc. of water and mark the stem on a level with the meniscus. Paraffin the stem which was connected with the stopcock, graduate it in millimeters beginning with the original mark, and etch the graduation into the glass. Finally, determine accurately the capacity of the graduated portion of the stem and of the bulb by weighing the water which they will deliver. For some purposes it is convenient to have both stems of the pipette graduated.

Directions are also given for the conversion of a full-pipette into one for the calibration of burettes.

Blow a small bulb — one holding less than 2 cc. — at a convenient distance from the end of the upper stem of a 50-cc. pipette. Make a mark on the stem between the bulb and the end, but quite near the bulb. Place the pipette in the arrangement represented in Fig. 16, and fill burette and pipette with water. Empty the pipette to the mark which was made below the little bulb, and then fill into the pipette from the burette, as exactly as may be, 2 cc. of water. Mark the stem on a level with the meniscus. Fill in, further, about 49.7 cc. of water. If that volume of water fills the large bulb and enters the stem above, no second mark between the two bulbs will be required, and the upper stem is to be marked on a level with the meniscus. If it does not enter the stem, attach a strip of gummed paper to the stem between the bulbs and empty the pipette to some point above the smaller bulb. Mark the place on the paper and again fill in 49.7 cc. of water from the burette. If the given volume of water now enters the upper stem, mark its limits on both stems and graduate the remainder of the upper one in millimeters. Finally, determine exactly the delivering capacity of the bulb and of the graduated stem.

The Graduation of Glass Tubes

The simple method of Bunsen (*Gasometrische Methoden*, 2. Auflage, p. 28) is to be recommended for the graduation in millimeters of tubes of all kinds. There are required for the work a thick board, 2 meters by about 2 decimeters, and a marking instrument resembling a beam compass.

The board is usually cut transversely into two pieces of equal length which are hinged together. It is also provided with a semicircular or V-shaped groove, running from end to end, to receive the standard graduated tube and the tube to be graduated. When instruments having bulbs are to be graduated, the wood may be cut away in the proper places to receive the bulbs and thus allow the tubes to lie on the bottom of the groove. On each side of the groove, at a distance of about 60 mm. from its center and parallel to it, is a row of six threaded brass posts. Each post is provided with a thumb nut and a strip of brass (75×30 mm.) which has been bent to right angles at a distance of 6 mm. from the ends. There are also four rectangular strips of brass (850×45 mm.) which, in conjunction with the short strips upon the posts, are employed to hold the tubes in place in the groove and to assist in guiding the graduation. One of the long edges of two of them is notched at points 5 mm. apart, the alternate notches being somewhat deeper than the others.

The wooden beam of the compass has a length of one meter; hence the curvature of the short lines cut by it is imperceptible. The point of the compass which is used in cutting away the wax should not be round in form but should resemble, rather, the cutting end of a woodworker's chisel.

The tube to be graduated, by warming and turning it over a flame, is carefully covered with a thin coat of beeswax or paraffin and laid into one end of the groove. The notched strips of brass are brought up on either side until the space between them is equal to the length of the lines to be cut and are then

fastened in place by means of the strips and nuts on the posts. A tube with a correct scale, e.g. a eudiometer, is fastened in a similar manner in the other end of the groove. One of the steel points of the compass is dropped into a line on the standard scale, and with the other a line is cut in the wax. The point is then dropped into the next groove and a second line cut, and so on until the graduation is completed. As is usual in a millimeter scale, the fifth and tenth lines, owing to the notching of the edges of the metallic strips, will be longer than the others, and the latter will be longer than the former. The tenth lines should be numbered, but in order that the reading of the numbers may be easy, the stylus with which they are engraved in the wax must not have a too fine point. If the wax has been scraped from the glass in places by the metallic



FIG. 17

strips, the injury may be repaired with the aid of a warmed knife blade or with a piece of hot glass.

The arrangement which has been described is the one usually employed in graduating ordinary eudiometers (Fig. 17). When smaller tubes are to be graduated, they must be raised above the groove by notched blocks which should have a length equal to the width of the board. These blocks should be provided with two holes or slots for the brass posts. If tubes attached to bulbs are to be graduated, notched metallic strips which are shorter than those mentioned will probably be required. In the place of the grooved and hinged board a half dozen notched blocks may be used. These should have a length of about 2 decimeters. The proper depth and also the size of the notch will be determined by the form and size of the apparatus to be graduated. Each block is provided with two threaded posts,

one upon either side of the notch, and with screws by which it may be fastened to a table top. To hold the apparatus in place and to guide the graduation, the metallic strips previously described may be used. It is desirable that the distances between the points of the compass should be adjustable. Some of the recent forms of the extension-beam trammels used by mechanics fulfill this condition most satisfactorily.

The graduation may be etched into the glass with a very concentrated solution of hydrofluoric acid, which is best applied with a swab of cotton wool attached to the end of a wire. If the graduated portion of the instrument is kept thoroughly wet with fresh quantities of the acid, an exposure of about two minutes is required for the proper etching of the scale. A somewhat better effect is obtained by using the acid in the dry, gaseous condition. A suitable bath for this purpose is easily made by lining a narrow wooden trough or box with sheet lead. A quantity of ground fluor spar is spread over the bottom of the trough and covered with concentrated sulphuric acid. The tube is placed on top and the part to be etched covered with a curved piece of sheet lead. To determine the length of time during which it is necessary to expose the apparatus in order to secure a satisfactory result, it is well, if practicable, to place a trial tube in the bath at the same time, which may be removed at intervals for the purpose of examining the lines

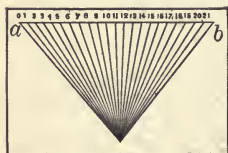


FIG. 18^a

with the finger nail. Tubes to be etched by the gaseous acid must be closed with corks, and the whole of the exposed exterior must be covered with wax.

If it is required to divide a fixed arbitrary length of tube into a given number of equal spaces, as happens when the graduation of burettes and similar apparatus is undertaken, Bunsen's arrangement represented in Fig. 18^a may be substituted for the standard millimeter scale. It consists of a system of converging lines etched on a plate of hard glass. Measured on the line *ab*,

or any line parallel to it, the converging lines are equidistant. Suppose now it is required to divide a length of 20 mm. into 15 equal spaces. A straight edge would be placed upon the plate parallel to ab and moved towards the apex until the distance between the first and the fifteenth line, measured on the straight edge, is equal to 20 mm., when it would be clamped to the glass. The straight edge would next be placed in line with the piece to be marked and the graduation transferred in the usual manner. It is somewhat difficult to secure and maintain the right relation between the straight edge and the base line ab ; it is therefore better to employ in the place of the Bunsen system of converging lines a system of equidistant parallel lines (Fig. 18^b). The intersections will then be equidistant whatever the position of the straight edge on the ruled plate.



FIG. 18^b

It is sometimes necessary to prepare for a special purpose a burette or other liquid-measuring apparatus which differs in some way from the instruments usually kept in stock. As a rule, the graduation of such pieces presents no great difficulty. We will suppose that the bulb tube represented in Fig. 19 is to be so graduated that the bulb, together with a short section of the upper and lower tubes, will deliver 100 cc. at 20°, while the remainder of the lower tube will deliver cubic centimeters at the same temperature. The directions for the operation would be as follows: Mark the point above the bulb at which it is desired to have the graduation



FIG. 19

begin and put the tube in the place of the burette in the arrangement represented in Fig. 16. Substitute for the pipette in the figure a 100-cc. calibrating pipette and find in the table which goes with the instrument how many stem divisions must be added to the capacity of the bulb if the instrument is to deliver 100 cc. at 20°. Fill both instruments with water and empty the pipette to the zero mark under the bulb.

Now allow the water to flow from the burette into the pipette until it has risen to the right height in the stem. Mark the tube under the bulb on a level with the meniscus. This will complete the graduation of the bulb. A little preliminary measuring may be necessary before commencing such a graduation in order to determine at what point it is best to locate the mark above the bulb.

For the graduation of the tube substitute for the pipette used in graduating the bulb a 5- or 10-cc. calibrating pipette, and find, as before, how many stem divisions must be filled for the delivery by the instrument of 5-cc. (or 10-cc.) volumes at 20°. Draw off exactly the required quantities and mark the tube after each withdrawal. Cover the tube with wax and — with the aid of one of the systems of lines previously described — graduate the spaces between the marks into tenths of a cubic centimeter. Finally, determine by a calibration of the instrument the errors of the graduation.

The marks made upon the tube during the graduation must lie, as nearly as possible, in the same vertical line. They should be very short also, and at the same time so distinct that afterwards they may be readily identified under the wax. The tube may be waxed before graduation, but in that case the covering must be thin or the tube will not be sufficiently translucent.

In using apparatus graduated to deliver certain volumes of liquids, it is assumed that a given area of glass surface always retains the same quantity of liquid when the apparatus is emptied, whereas the quantity retained may vary somewhat according to the character of the liquid and the condition of the surface. Instruments of this kind should be thoroughly cleansed, first with an alcoholic solution of potassium hydroxide and then with distilled water. Grease of any kind upon the glass causes that portion of the liquid which should remain uniformly distributed over the surface to collect in drops, and it is

by no means certain that the quantity of liquid in these will be equal to that which would normally cling to the clean glass. Hence the interior of burettes and of other liquid-measuring apparatus should not be wiped with cloths, paper, or other material likely to contain any oily matter. The practice of rinsing with ether is likewise unsatisfactory because the ordinary commercial ether often contains in solution fats or gums which, after evaporation of the ether, are left upon the glass. Sometimes, in spite of the most thorough cleansing, the liquid film persists in breaking and collecting in drops. In such cases the difficulty cannot be remedied since it is apparently due to the character of the glass surface and not to any deposit of foreign material upon it.

Care should be taken, when measuring from a burette, not to allow it to deliver too rapidly, otherwise more than the normal quantity of liquid will be left temporarily upon the glass, and the reading, if taken immediately, will be erroneous. If there is any reason to fear an error from this cause, the correctness of the reading should be confirmed by a later one.

The correct reading of burettes is greatly facilitated by the use of the Erdmann float. The float should be neither so large as to stick in any part of the tube, nor so small that it can assume any other than a vertical position in the liquid.

Standard and Normal Solutions

A *standard* solution is one whose concentration has been regulated with a view to its convenient use in determining other substances. For example, a solution of potassium permanganate of such concentration that one cubic centimeter of it will convert five milligrams of iron from the ferrous to the ferric condition is a standard solution; likewise a solution of sodium chloride for the determination of silver, one cubic centimeter of which will precipitate ten milligrams of silver. Any solution used in volumetric work whose concentration is known

or whose equivalence, with respect to the substances which may be determined by it, has been ascertained, is a standard solution.

Normal solutions are standard solutions which are peculiar in this respect, that the standard determining their concentration is of such a character that equal volumes of different solutions are *chemically equivalent*. The definitions for normal solutions which are now generally accepted are the following:

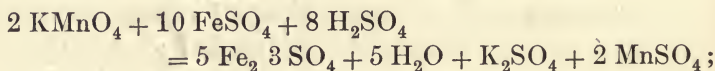
1. A normal solution of an acid is one which contains in a liter-volume one gram of replaceable hydrogen.

2. A normal solution of a base is one which contains in a liter-volume that quantity of the basic metal which will replace one gram of acid hydrogen.

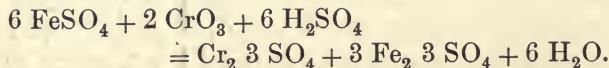
3. A normal solution of a salt is one which contains in a liter-volume that quantity of salt which is formed by the replacement of one gram of acid hydrogen by the metal of a base.

A liter-volume of a normal mono-basic acid, or of a normal mono-acid base, contains the number of grams of the dissolved substance which is equal to the molecular weight of the substance; while a normal solution of a bi-basic acid, or of a bi-acid base, contains in a liter the number of grams of the dissolved substance which is equal to one-half the molecular weight of the substance; etc.

Standard solutions of certain salts — for example, potassium permanganate and ferrous sulphate — are employed in volumetric work for purposes of oxidation and reduction; as when iron is determined in accordance with the reaction



and chromic acid in accordance with the reaction



The question arises, What are to be considered as *normal* solutions in such cases? According to the definitions previously given, a normal solution of potassium permanganate—regarding

the substance as a salt of the mono-basic acid HMnO_4 — would contain in a liter-volume the number of grams of the substance which is equal to its molecular weight. But a liter of such a solution, acting as an oxidizing agent, would be equivalent to 5 grams of hydrogen. Again, since ferrous sulphate is a salt of a bi-basic acid, a normal solution of it, according to the definition, would contain in a liter-volume the number of grams of the substance which is equal to one-half its molecular weight. But as a reducing agent, a liter of such a solution would be equivalent only to one half gram of hydrogen. On the whole, it appears more rational to emphasize the purpose for which such solutions are used rather than their classification as salts; and to adopt, therefore, the following definitions with reference to them:

1. A normal solution of any substance employed as an oxidizing agent is one containing in a liter-volume the quantity of active oxygen which is required to convert one gram of hydrogen into water.

2. A normal solution of any substance employed as a reducing agent is one having in a liter-volume a reducing power equal to that of one gram of hydrogen. According to the definitions here given, a normal solution of potassium permanganate would contain in a liter-volume the number of grams of the salt which is equal to one-fifth its molecular weight; while a normal solution of ferrous sulphate would contain in the same volume the number of grams of the salt which is equal to its molecular weight.

The principal advantage in using normal solutions in volumetric work lies in the fact that a general system based on the atomic and molecular weights of the substances employed greatly simplifies the computation of the quantitative results of all chemical reactions in which those substances take part. In using standard solutions for the determination of other substances, the effect of unavoidable errors of measurement upon the correctness of the results is proportional to the concentration

of the solutions. It is therefore customary in work requiring any considerable degree of accuracy to employ very dilute solutions. Normal solutions are diluted to one-tenth, and in some instances to one-hundredth, of their concentration. The decimal plan of dilution is adopted because it does not sensibly diminish the advantage of the normal system.

Normal solutions are to be carefully distinguished from the *gram-equivalent* solutions which are much used in the determination of molecular weights by certain modern methods. A gram-equivalent solution always contains in a liter the number of grams of the dissolved substance which is equal to the molecular weight of the substance. Such solutions are equi-molecular or molecular-equivalent, that is, equal volumes of them contain the same number of molecules; but the equal volumes are not, as in the case of normal solutions, necessarily *chemically equivalent*. Some confusion has arisen from the practice of calling gram-equivalent solutions normal solutions. Perhaps the distinction between the two classes of solutions could be emphasized with advantage by calling the one volume-normal, and the other molecular-normal.

The Correction of Standard Solutions for Temperature

All volumetric apparatus should be graduated or calibrated for the particular temperature which usually prevails in the laboratory in which the instruments are to be used. The standard solutions also should be so made up as to be correct at the standard temperature; and they should be used, as far as practicable, at that temperature. But, since the temperature of every laboratory is subject to considerable variations, it is often necessary both to make and to use the standard solutions at other than the standard temperature. The errors which arise from this source are usually tolerable in ordinary volumetric work, but they require attention whenever any considerable degree of accuracy is sought. Such corrections, though seeming to

involve laborious computations, can be easily and expeditiously made with the aid of a very simple device which will now be explained.

In estimating the magnitude of the errors which result from measuring standard solutions at other than standard temperatures, two things must be taken into account, — the expansion or contraction of the liquids and the expansion or contraction of the measuring instruments. The errors of the measurements are equal to the differences between the two. We will suppose, for purposes of explanation, that the standard temperature is 20° , and that water is the liquid to be dealt with. The reason for selecting water instead of a solution will appear hereafter. The problem is to devise some expeditious method of finding what volumes quantities of water measured at other temperatures would have if measured at the standard temperature of 20° ; or, if need be, for finding what volumes quantities of water measured at 20° would have if measured at other temperatures. We will suppose that the extreme limits to be provided for are 10° on the one side and 30° on the other. The following table gives the volumes of water at 10° , 15° , 25° , and 30° as compared with its volume at 20° .

TABLE I

10°	15°	20°	25°	30°
0.998511	0.999098	1.000000	1.001142	1.002503

Table II gives the volumes which a liter of water, measured at 20° , would have at 10° , 15° , 25° , and 30° , and the amounts of the contraction or expansion.

TABLE II

10°	15°	20°	25°	30°
998.511 cc.	999.098 cc.	1000.000 cc.	1001.142 cc.	1002.503 cc.
1.489 cc.	0.902 cc.	0.000 cc.	1.142 cc.	2.503 cc.

Suppose a graduated glass vessel holding exactly one liter at 20° is filled with water also having a temperature of 20° . The

volume of the water will be 1000 cc. If now the temperature of the water falls to 10° , its volume will be 998.511 cc. (see Table II). But the water will not measure that amount by the graduation of the vessel because the latter has also diminished in size by $1000 - \frac{1000}{1.00025}$, that is, by 0.25 cc. It will appear to have a volume of $\frac{998.511}{1 - .00025}$, or 998.761 cc.; and $1000 - 998.761$, or 1.239 cc., is the value of the correction which must be added to the apparent volume to find what the volume of the water would be at 20° , — the standard temperature.

If, on the other hand, the temperature of the water rises to 30° , its true volume will be 1002.503 cc.; but it will measure less than that in a graduated vessel which is correct at 20° because the vessel has also suffered expansion. Its apparent volume will be $\frac{1002.503}{1.00025}$, or 1002.252 cc.; and $1002.252 - 1000$, or 2.252 cc., is the correction which must be deducted from the apparent volume of the water at 30° in order to find what its volume at 20° would be. Table III gives the values of the corrections for one liter of water at 10° , 15° , 25° , and 30° . We should obtain values sufficiently near the truth for all ordinary purposes by simply subtracting the contraction or expansion of a liter measuring flask from the absolute contraction or expansion of a liter of water as given in Table II.

TABLE III

10°	15°	25°	30°
+ 1.239 cc.	+ 0.777 cc.	- 1.017 cc.	- 2.253 cc.

For convenience of use in practice a curve of corrections is to be made for each degree between 10° and 20° on one side and between 20° and 30° on the other. To prepare the curves a horizontal line upon the cross-ruled paper is made to represent cubic centimeters of liquid from 0 cc. to 100 cc. A vertical line at the 100 cc.-end of the horizontal one, and extending above

and below it, is employed for the corrections to be applied to a 100 cc.-volume at different temperatures; the upper portion being reserved for positive quantities and the lower one for negative quantities. Each space on the vertical line is made to represent 0.01 cc. Hence we cut off on the upper portion of it 12.4 spaces to represent the contraction from 20° to 10° , and on the lower portion 22.5 spaces to represent the expansion from 20° to 30° . Each of these two intervals is then divided into ten equal parts labeled 19° , 18° , 17° , . . . , 10° from the base line upwards, and 21° , 22° , 23° , . . . , 30° from the base line downwards. Finally, the temperature points upon the vertical line are joined by straight lines to the zero end of the horizontal line. With the aid of such a figure one can determine by a simple inspection how much is to be added to or subtracted from any volume of water not exceeding 100 cc., when measured at any temperature between 10° and 30° , in order to find what volume it would occupy at 20° ; or he may ascertain with equal ease what volume water measured at 20° would appear to have if measured at any other temperature within the given limits.

Correction curves prepared in accordance with the plan here developed are not rigidly accurate. The expansion of water has been assumed to be uniform between 10° and 20° on the one hand, and between 20° and 30° on the other, which is not in accordance with the truth. Again, the expansion of glass has been assumed to be regular between 10° and 30° , which is also not strictly correct. The errors resulting from the former assumption are not large and they may be easily avoided by dividing the vertical or temperature line of the correction figure in accordance with the known irregularities of the expansion of water. The effect of the irregularities of the expansion of glass is of no significance since it never amounts to quantities which can be measured by ordinary volumetric apparatus.

The figures employed for the correction of liquid volumes for temperature may, of course, be drawn upon a larger scale

than that proposed above, and for larger volumes of the liquid, e.g. a liter instead of 100 cc.

The expansion of glass and of water, the usual solvent, has been investigated with care, but the expansion coefficients of solutions of the concentration usually employed in volumetric analysis have not, unfortunately, been determined to any great extent. It is often assumed for purposes of correction that these dilute solutions expand and contract with changing temperatures to about the same extent as water itself. But, judging by the results of an investigation by Alfred Schulze (*Zeitschrift für analytische Chemie*, **21**, 167), the assumption is justified only in the case of very dilute solutions, — solutions, for example, of $\frac{1}{10}$ normal concentration. Schulze determined the expansion of $\frac{1}{10}$ normal solutions of sodium chloride and silver nitrate from 0° to 30°. His results, together with the corresponding figures for water, are given for certain intervals of temperature in the following table.

TABLE IV

	0°	10°	15°	20°	25°	30°
Water	1.000000	1.000124	1.000712	1.001615	1.002759	1.004123
$\frac{N}{10}$ NaCl	1.000000	1.000360	1.001030	1.001965	1.003160	1.004630
$\frac{N}{10}$ AgNO ₃	1.000000	1.000398	1.001075	1.002032	1.003240	1.004690

In the next table the volumes of the three liquids at 10°, 15°, 25°, and 30° are compared with their volume at 20°.

TABLE V

	10°	15°	20°	25°	30°
Water	0.998511	0.999098	1.000000	1.001142	1.002503
$\frac{N}{10}$ NaCl	0.998398	0.999066	1.000000	1.001192	1.002659
$\frac{N}{10}$ AgNO ₃	0.998369	0.999044	1.000000	1.001205	1.002652

If we subtract the numbers in the above table from unity and multiply the differences by 1000, and then deduct the expansion

of a liter flask from 10° and 15° to 20° , and from 20° to 25° and 30° , we shall obtain the quantities which would be used in constructing for a liter-volume of each of the three liquids a correction figure like that already explained. Table VI gives these quantities.

TABLE VI

	10°	15°	25°	30°
Water	+ 1.239 cc.	+ 0.777 cc.	- 1.017 cc.	- 2.253 cc.
$\frac{N}{10}$ NaCl	1.352	0.809	1.067	2.409
$\frac{N}{10}$ AgNO ₃	1.381	0.831	1.080	2.402

Judging by the evidence afforded by this table, it is probably safe to employ the known expansion of water for the correction of solutions of tenth-normal concentration; for with a standard temperature of 20° , the maximum error which could result from so doing would amount in measuring a liter-volume of $\frac{N}{10}$ silver nitrate to only 0.142 cc. at 10° , 0.054 cc. at 15° , 0.063 cc. at 25° , and 0.149 cc. at 30° ; while the error in measuring an equal volume of $\frac{N}{10}$ sodium chloride solution would amount to only 0.113 cc. at 10° , 0.032 cc. at 15° , 0.05 cc. at 25° , and 0.156 cc. at 30° . The maximum error in the correction for a measurement of 50 cc. of either liquid would amount to less than 0.01 cc.

Schulze also determined the expansion of six normal solutions from 0° to 30° . The results for several intervals of temperature, together with the corresponding volumes of water, are given on the following page.

TABLE VII

	0°	10°	15°	20°	25°	30°
Water	1.000000	1.000124	1.000712	1.001615	1.002759	1.004123
Oxalic acid	1.000000	1.000993	1.001940	1.003125	1.004560	1.006168
Hydrochloric acid	1.000000	1.001010	1.001905	1.003013	1.004328	1.005850
Nitric acid	1.000000	1.001800	1.003050	1.004490	1.006120	1.007933
Sulphuric acid	1.000000	1.001720	1.002945	1.004385	1.005990	1.007820
Sodium carbonate	1.000000	1.001880	1.003130	1.004565	1.006165	1.007955
Sodium hydroxide	1.000000	1.002050	1.003365	1.004848	1.006510	1.008330

The expansion of the six normal solutions included in the table diverges more from that of water at temperatures below 10° than above. This will appear more clearly if we select 20° instead of 0° as our standard temperature, as is done in the following table.

TABLE VIII

	10°	15°	20°	25°	30°
Water	0.998511	0.999098	1.000000	1.001142	1.002503
Oxalic acid	0.997874	0.998818	1.000000	1.001430	1.003033
Hydrochloric acid	0.998003	0.998895	1.000000	1.001311	1.002828
Nitric acid	0.997322	0.998566	1.000000	1.001622	1.003427
Sulphuric acid	0.997346	0.998566	1.000000	1.001598	1.003420
Sodium carbonate	0.997327	0.998571	1.000000	1.001592	1.003374
Sodium hydroxide	0.997215	0.998524	1.000000	1.001653	1.003465

If the quantities in Table VIII are treated as were those in Table V in order to secure the data required for the construction of a correction figure for each of the liquids, we obtain the following results.

TABLE IX

	10°	15°	25°	30°
Water	+ 1.239 cc.	+ 0.777 cc.	- 1.017 cc.	- 2.253 cc.
Oxalic acid	1.876	1.057	1.305	2.783
Hydrochloric acid	1.747	0.980	1.186	2.578
Nitric acid	2.428	1.309	1.497	3.177
Sulphuric acid	2.404	1.309	1.473	3.170
Sodium carbonate	2.423	1.304	1.467	3.124
Sodium hydroxide	2.535	1.351	1.528	3.215

It appears from the values recorded in Table IX that the known expansion of water cannot be employed for the correction of standard solutions of normal concentration. Up to the present time we have the necessary data for the temperature correction of only the six normal solutions included in the above table. As a temporary expedient, however, it is probably safe to employ for normal solutions of unknown expansion the mean values of the corrections in Table IX. For a liter-volume these are:

TABLE X

10°	15°	20°	25°	30°
+ 2.236 cc.	+ 1.218 cc.	0.000 cc.	- 1.409 cc.	- 3.008 cc.

We have to consider now the course to be followed when a standard solution is to be made at some other than the standard temperature. We will suppose that the standard temperature is 20° and that a tenth-normal solution of sodium chloride is to be made at 15° in a liter flask, which is correct, of course, only at 20°. At 15° the flask will hold not a liter, but $1.000 \div 1.000125$, or 999.875 cc., and this will be the true volume of the solution when made up at the given temperature. We wish now to find what its volume at 20° will be. For this purpose we assume that the expansion of tenth-normal solutions is about equal to that of water. If the volume of water at 20° is 1.0, its volume at 15° is 0.999098 (see Table I); therefore 999.875 cc. of the solution measured at 15° will become $999.875 \div 0.999098$, or 1000.778 cc., at 20°. A liter of the solution should contain at the standard temperature 5.806 grams of the salt, and a cubic centimeter 0.005806 gram. The weight of the salt to be dissolved at 15° is therefore 0.005806×1000.778 , or 5.8105 grams.

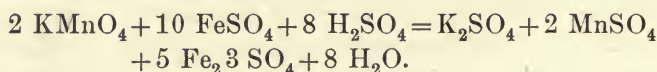
Suppose, on the other hand, that the temperature at which the solution is to be made is 25°. The flask will then have a capacity of 1.000×1.000125 , or 1000.125 cc., and this will be the volume of the solution when made. Its volume at 20° will be $1000.125 \div 1.001142$, or 998.98 cc. The quantity of the salt to be weighed out is therefore 998.98×0.005806 , or 5.8001 grams.

CHAPTER V

THE PREPARATION OF STANDARD SOLUTIONS OF ACIDS AND ALKALIES

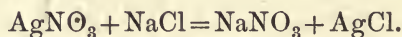
INDICATORS

When a standard solution of potassium permanganate is allowed to flow from a burette into a solution of ferrous sulphate to which a little sulphuric acid has been added, the following reaction takes place:



As long as there remains any ferrous salt in the solution, the permanganate is reduced and loses, in consequence, its characteristic color. As soon, however, as the reaction with the iron is finished, the reduction ceases, and an additional drop of the permanganate — or even a fraction of a drop if the volume of the liquid is not large — imparts a distinct rose color to the solution. The sudden appearance of the color is so striking that one is always able to determine with great precision the point at which the reaction between the permanganate and the ferrous iron is finished.

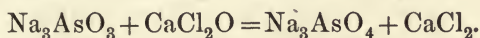
If a standard solution of silver nitrate is added in the same way to a solution of any chloride, the chlorine is precipitated as silver chloride,



But since the solution of silver nitrate is colorless, and the freshly formed silver chloride is slow in subsiding, it is difficult to determine when the precipitation is completed. If, however, in the beginning, there are added to the solution of chloride a

few drops of a solution of neutral potassium chromate, the precipitation of silver chloride will proceed as before, and there will be no permanent reaction between the silver nitrate and the chromate until the precipitation of the chlorine is finished. There will then appear in the solution a permanent red color due to the formation of silver chromate, which is a sufficient indication that enough of the standard solution has been added.

Again, if a solution of sodium arsenite is added to one of bleaching powder, the arsenite will be converted into arseniate,



But nothing will occur in the solution to indicate when the reaction is finished. If, however, a drop of the liquid is removed upon the end of a glass rod from time to time, and applied to a piece of filter paper which has been dipped in a solution of starch and potassium iodide and then dried, it is easy to ascertain when the last trace of hypochlorite disappears; for as long as any of it is present a blue spot will appear whenever the paper is touched with a drop of the liquid.

Substances which, like potassium chromate in the determination of chlorine by a standard solution of silver nitrate, and like the mixture of potassium iodide and starch in the determination of a hypochlorite by sodium arsenite, are employed to indicate the completion of reactions are called indicators. Only those which are most frequently used in connection with the neutralization of acids and bases need be considered in this place.

1. LITMUS

Preparation. The crushed commercial litmus is repeatedly extracted with fresh quantities of boiling 85 per cent alcohol for the purpose of removing a violet coloring matter which is reddened by acids but not made blue by alkalies. The residue, consisting mainly of calcium carbonate, carbonates of the alkalies, and the substance to be isolated, is washed with more hot

alcohol upon a filter, and then digested for several hours with cold distilled water. The filtered aqueous extract has a pure blue color and contains an excess of alkali, a part of which is in the form of carbonate and a part in combination with the litmus. To remove the alkaline reaction, the solution is heated to the boiling point and cautiously treated with very dilute sulphuric acid until it becomes distinctly and permanently red. The boiling must be continued until the carbonic acid which is liberated in the solution has been expelled, otherwise the blue color may reappear after a time. The red solution, after expulsion of the carbonic acid, is treated with a dilute solution of barium hydroxide until the color changes to a violet, and is then filtered. In this state the solution is very sensitive to acids or alkalies, changing to red with the former and to blue with the latter.

In closed vessels the solution soon loses color and acquires an offensive odor. But if a solution which has been thus altered is exposed to the air in shallow vessels, it soon regains its original color. Solutions of litmus should therefore be kept in open and only partly filled bottles. Paper caps placed over the necks of the bottles will protect the solutions from dust and at the same time admit the air which is necessary for their preservation.

In neutralizing an acid with an alkali, the quantity of the latter which must be added is somewhat more than equivalent to the quantity of the former, since a small amount of the alkali is required to give the litmus a blue color. For the same reason, when an alkali is neutralized, a slight excess of the acid must be added. Hence the importance of making the indicator as sensitive as possible in the beginning. There are two remedies for the difficulty. The litmus solution may be divided into two parts, one of which is changed to a red color with the least possible quantity of acid, and the other to a blue with the least possible quantity of alkali. When now an acid is to be neutralized with a standard alkali, the blue solution is employed as the

indicator and vice versa. Or, one may apply a so-called color correction. The magnitude of this correction is ascertained by adding to a quantity of neutral water, equal in volume to the solution of acid or alkali, the same amount of the indicator that is to be used in the neutralization experiment, and then finding how much of the standard solution is required to produce the required color.

If preferred, the litmus may be precipitated and preserved in solid form. For this purpose the solution, prepared as described above, is evaporated to a small volume and then treated with strong alcohol. The precipitate is collected on a filter, washed with alcohol, and dried over calcium chloride.

Litmus is a satisfactory indicator with the following substances:

1. Hydrochloric, hydrobromic, sulphuric, nitric, and oxalic acids.
2. The hydroxides of the alkaline and alkaline earth metals and ammonia.
3. The arsenites and silicates of the alkalies.
4. The carbonates and sulphides of the alkalies and alkaline earths in boiling solutions.

Its conduct is unsatisfactory:

1. With sulphurous, phosphoric, arsenic, boric, and chromic acids.
2. With most organic acids.
3. With carbonates and sulphides in cold solutions.

2. PHENOLPHTHALEIN

Preparation. Half a gram of the solid material is dissolved in 100 cc. of neutral 95 per cent alcohol. If the alcohol is found to have an acid reaction, as it often has, it should be boiled for a short time. If its acid reaction does not disappear after boiling, the alcohol should be agitated with dry calcium hydroxide (slaked lime) and redistilled.

Phenolphthalein is nearly colorless in neutral and acid solutions and red in those containing the least excess of alkali. It is a delicate indicator:

1. For the hydroxides of the alkaline and alkaline earth metals.

2. For most mineral acids.

3. For most organic acids.

Its conduct is unsatisfactory:

1. With ammonia and in solutions containing ammonium salts.

2. With arsenious, silicic, and boric acids.

Phenolphthalein is exceedingly sensitive to carbonic and sulphhydric acids, but exhibits a neutral reaction as soon as their acid salts have been formed. With phosphoric and arsenic acids it exhibits a neutral reaction when two-thirds of their acid hydrogen has been replaced. In this respect it differs from litmus, toward which the mono-hydrogen phosphates and arseniates of the alkaline metals are alkaline, and the di-hydrogen salts neutral.

3. METHYL ORANGE

Preparation. One part of the dyestuff is dissolved in a thousand parts of cold distilled water. Ordinarily not more than two or three drops of this dilute preparation should be added to a solution in which a determination is to be made.

In very dilute neutral or alkaline solutions methyl orange has a yellow color which changes to a pink in the presence of the least excess of one of the stronger mineral acids. It owes its great value as an indicator not to any superior sensitiveness, but principally to the fact that it is almost wholly indifferent to carbonic and sulphhydric acids, and to certain salts which give an acid reaction with litmus and some other indicators. It is also indifferent to arsenious, boric, silicic, and hydrocyanic acids, which makes it practicable to determine volumetrically the bases in combination with these weak acids.

Methyl orange may be used as an indicator in the determination of the following substances :

1. The stronger mineral acids.
2. The hydroxides of the alkaline and alkaline earth metals.
3. Ammonia.
4. The bases in such carbonates, sulphides, arsenites, silicates, and borates as are decomposed by dilute nitric, hydrochloric, or sulphuric acid.
5. Phosphoric and arsenic acids which become neutral to methyl orange when one-third of their hydrogen has been replaced.
6. Sulphurous acid which becomes neutral to the indicator with the formation of its acid salt.

Methyl orange cannot be used for the determination of organic acids, or in solutions containing nitrous acid or nitrites which destroy it. Moreover, it cannot be employed in hot solutions.

4. TROPÆOLIN

The dyestuff known as tropæolin No. 00 conducts itself towards acids and alkalies like methyl orange.

5. COCHINEAL

Preparation. Commercial cochineal is reduced to a coarse powder and digested with from 10 to 20 parts of 25 per cent alcohol.

In neutral and acid solutions cochineal has a yellowish-red color, which changes to a violet in the presence of alkali. Towards the stronger mineral acids and the hydroxides of the alkaline and alkaline earth metals it is quite sensitive. It is of little value in the titration of organic acids, and cannot be used in solutions containing acetates, salts of copper, or any traces of iron or aluminium. It can be used by gaslight with very satisfactory results.

EXERCISE X

THE PREPARATION OF STANDARD SOLUTIONS OF ACIDS
AND ALKALIES

I. BY MEANS OF OXALIC ACID

a. Preparation of Pure Oxalic Acid

Agitate commercial oxalic acid in a closed bottle with a mixture of equal parts of ether and 95 per cent alcohol until the liquid is fully saturated with the acid. Filter into a flask through a plaited paper. Partly immerse the flask in a water bath, connect it with a condenser and receiver, and then heat as long as a copious distillate is obtained. To the distillate, which consists mainly of ether, add more alcohol, and with the mixture extract more of the acid. Filter and distill as before. When enough of the acid has been extracted, and its solution freed from ether, add to the residue an equal volume of distilled water which is free from ammonia and concentrate upon the water bath in a porcelain dish until the odor of ethyl oxalate and alcohol disappears and the solution is ready to crystallize on cooling. If the odor of ethyl oxalate or alcohol has not wholly disappeared when the solution becomes sufficiently concentrated for crystallization, more water must be added and the evaporation repeated. Stir the solution while the crystals are forming. Collect the acid in a funnel in the bottom of which a perforated porcelain disk or a platinum cone has been placed. Remove as much as possible of the mother liquor with the aid of a filter pump, and spread the acid to dry upon a clean unglazed porcelain plate. Burn a quantity of the acid upon the lid of a platinum crucible, or in a dish of the same material, to find whether or not it leaves a weighable residue.

Commercial oxalic acid contains acid oxalates from which it cannot be readily freed by the ordinary process of recrystallization from water. The difficulty in removing the salts by this

method is due to the fact that the acid oxalates, though readily dissolved by hot water, are only very moderately soluble in cold water. Hence they are reprecipitated from cooling saturated solutions of the acid. A partial removal of the salts may be effected by saturating cold water with the acid and then evaporating to the point of crystallization.

The air-dried acid is neither deliquescent nor efflorescent in air containing the usual amount of moisture. It cannot be dried in a desiccator, since in an atmosphere devoid of moisture it loses water of crystallization. Its solutions are not altogether stable.

b. Preparation of a Tenth-Normal Solution of Oxalic Acid

Oxalic acid is bi-basic and has a molecular weight of 125.08. It would therefore be necessary, in order to prepare a liter of the normal solution, to weigh out $\frac{125.08}{2}$, or 62.54 grams of the pure acid. To prepare a liter of a tenth-normal solution, one-tenth of this quantity, or 6.254 grams, would be required. One half-liter of the latter solution will suffice for the present exercise. This will require 3.127 grams of the acid. The weighing of fixed quantities, however, consumes much time. It is therefore better to proceed as follows: Weigh out a few milligrams more than the required amount of the acid. Dissolve it in distilled water, free from ammonia and carbonic acid; transfer the solution to a half-liter flask, taking care not to wet the neck; rinse the vessel in which the solution was made several times with water and pour the rinsings into the flask. Add more water, a little at a time, mixing the contents of the flask after each addition, without wetting the neck, until the flask is nearly full. Now fill to the mark, close the flask, and mix the liquid thoroughly. The solution will be somewhat too concentrated. Divide the weight of acid required for a half-liter, i.e. 3.127 grams, by the weight of the acid in one cubic centimeter of the solution. This will give the number of cubic

centimeters which must be diluted to half a liter, and the difference between that number and 500 will be the volume of water required for the dilution. With a pipette remove a quantity of the solution, add the required volume of water, and then fill the flask to the mark with a portion of the solution which was removed to make room for the water.

The plan here proposed for making solutions of definite concentration from weighed quantities of substances has various advantages over that of weighing out exactly the required amounts of the substances to be dissolved. The most important of these are the saving of time and the avoidance of long exposure of the material to the atmosphere at the time of weighing. Such exposure at the balance of powdered materials, or of those which absorb water or carbonic acid, is a serious obstacle in the way of obtaining correct weighings.

There is one error in the process which requires attention when the solutions to be made are of considerable concentration. It is assumed that the final volume of the liquid is equal to the sum of the volumes of the solution diluted and of the water which is added to it, whereas, in the case of aqueous solutions, dilution is usually attended by contraction. The effect of the error upon tenth-normal solutions is unimportant, and in the case of more concentrated solutions it may be reduced to insignificance by weighing out only very little more than the required amount of the substances to be dissolved.

Distilled water usually contains ammonia and carbonic acid, both of which must be removed before it is used in making standard solutions of acids. Therefore the water which is to be employed for this purpose should be vigorously boiled for 20 or 30 minutes and then allowed to cool to the standard temperature. Carbonic acid in the water with which standard solutions of acids are made increases the acidity and interferes with the normal conduct of such indicators as litmus and phenolphthalein; while ammonia, under the same conditions, weakens the acids and strengthens the standard alkalies. If only those

indicators are used which are indifferent to carbonic acid, the presence of that acid is, of course, unobjectionable. But standard acids which are made up with water containing considerable carbonic acid will exhibit different concentrations when neutralized with an alkali, according as litmus or phenolphthalein on the one hand, or methyl orange on the other, is used as the indicator. It is therefore advisable to expel the carbonic acid and ammonia from all water which is to be used in connection with neutralization experiments. The boiling of the water for this purpose should take place in porcelain vessels, since hot water extracts alkali from all varieties of glass which are used in a chemical laboratory, and from some of them with astonishing rapidity. This source of error in acidimetric work should not be overlooked. Beakers, flasks, and other glass vessels should be tested with regard to their fitness for use in such experiments. This may be done by boiling in them for an hour or more water having, in the beginning, a neutral reaction; and then determining — with the aid of phenolphthalein and a very dilute standard acid — whether an appreciable amount of alkali has been dissolved.

The common practice of employing compressed air from the lungs to force from a wash bottle the water which is required for dilution or other purposes is, of course, inadmissible in volumetric work with acids and bases.

c. Preparation of a Tenth-Normal Alcoholic Solution of Potassium Hydroxide

Dissolve two or three grams of sodium hydroxide in a liter and a half of 95 per cent alcohol and redistill. This treatment will free the alcohol from carbonic and other acids which the commercial material usually contains, and also from aldehydes and a substance extracted from the oak barrel staves, both of which when treated with alkali give a yellow color to the alcohol.

Dissolve about 3.3 grams of the purest obtainable potassium hydroxide in a half-liter of the redistilled alcohol, and set the solution aside in a glass-stoppered bottle. At first the solution will be cloudy from the presence in it of insoluble potassium carbonate, but this soon subsides and becomes firmly attached to the glass, leaving the solution of hydroxide quite clear.

With the room and the solutions at very nearly the standard temperature, fill one burette with the tenth-normal oxalic acid, and another with the alcoholic caustic potash. Cover both burettes with inverted test tubes. Measure into an Erlenmeyer flask 25 cc. of the standard acid and add to it a few drops of a solution of phenolphthalein which has also been made with the redistilled alcohol. Titrate the acid with the alkali until the red color appears and then determine whether a measurable quantity of the acid is required to destroy it. Titrate back and forth with the two solutions until a point is reached where the quantities of alkali and acid required to produce and destroy the color cannot be measured upon the burettes. Repeat the experiment. If the first and second results agree, calculate from the ascertained relation of the two solutions how many cubic centimeters of the alkali will be required to make a half-liter of a tenth-normal solution. Measure into a 500-cc. flask the volume of alcohol necessary for dilution, and fill to the mark with the alkali. Compare the diluted solution with the standard oxalic acid. They should be found equivalent; volume for volume.

The principal objection to the use of phenolphthalein as an indicator is its extreme sensitiveness to carbonic acid. Solutions containing it which have been reddened by the addition of a slight excess of an alkaline hydroxide soon lose their color in the air in consequence of the absorption of carbon dioxide. Even the breath of the operator is often a source of difficulty in a titration when this indicator is used. The evil is partially remedied by using flasks instead of beakers,

and by titrating, whenever practicable, into hot instead of cold solutions.

Alcoholic solutions of the alkaline hydroxides are not stable and must therefore be frequently restandardized. They soon turn yellow and then reddish-brown in consequence, apparently, of the absorption of oxygen and the formation of aldehyde resin. Any moderate development of color does not, however, interfere with their use in neutralizing acids. The principal advantage in using an alcoholic rather than an aqueous solution of an alkaline hydroxide lies in the fact that the alkaline carbonates, being nearly insoluble in concentrated alcohol, separate from the former as fast as they are formed in consequence of unavoidable exposure of the solutions to the air. In other words, alcoholic solutions of the caustic alkalies keep themselves free from carbonates and therefore in fit condition for use with indicators which, like litmus and phenolphthalein, are sensitive to carbonic acid.

Aqueous solutions of the alkaline hydroxides which are practically free from carbonates may be prepared by saturating so-called absolute alcohol with the solid caustic alkalies and then diluting the alcoholic solutions, after subsidence of the insoluble matter, with water. In such solutions any carbonate which may be subsequently formed in consequence of exposure to the air will, of course, remain in solution.

Aqueous solutions of the caustic alkalies may be freed from carbonates by adding to them a little hydroxide of calcium or of barium. But such solutions, as will be explained hereafter, cannot, under certain conditions, be used in conjunction with oxalic acid.

The great change in volume which alcohol suffers when its temperature is raised or lowered constitutes an objection to the employment of alcoholic solutions in volumetric work. Care must be taken both to make and to use such solutions at the standard temperature. Otherwise corrections must be applied to the measurements.

If the volume of alcohol (96 to 97 per cent) at 0° is represented by unity, its volume at any higher temperature t will be found by the formula

$$1 + at + bt^2 + ct^3, \text{ in which}$$

$$a = 0.00104139$$

$$b = 0.0000007836,$$

$$c = 0.000000017618.$$

The following table gives the volumes of alcohol, also those of water at several temperatures.

TABLE I

	0°	10°	15°	20°	25°	30°
Alcohol	1.000000	1.010510	1.015857	1.021282	1.026799	1.032423
Water	1.000000	1.000124	1.000712	1.001615	1.002759	1.004123

The next table gives the volumes of alcohol and of water at 10° , 15° , 25° , and 30° as compared with their volumes at 20° .

TABLE II

	10°	15°	20°	25°	30°
Alcohol	0.989452	0.994688	1.000000	1.005403	1.010908
Water	0.998511	0.999098	1.000000	1.001142	1.002503

Table III gives, in cubic centimeters, the decrease in volume of a liter of alcohol and of a liter of water when their temperature falls from 20° to 15° and 10° ; and their increase in volume when the temperature rises from 20° to 25° and 30° .

TABLE III

	10°	15°	20°	25°	30°
Alcohol	10.55 cc.	6.31 cc.	0.00 cc.	5.40 cc.	10.91 cc.
Water	1.49 cc.	0.90 cc.	0.00 cc.	1.14 cc.	2.50 cc.

If we deduct from the volumes given in the first horizontal line of the table the contraction of a liter flask from 20° to 15° and 10° and its expansion from 20° to 25° and 30° , we shall obtain the data required for the preparation of a correction figure (see page 104) to be used in connection with strong alcohol

or with weak solutions of alkalies in concentrated alcohol. Table IV gives these differences.

TABLE IV

10°	15°	20°	25°	30°
10.3 cc.	6.185 cc.	0.00 cc.	5.275 cc.	10.66 cc.

d. Preparation of a Tenth-Normal Solution of Hydrochloric Acid

Dilute 25 cc. of concentrated chemically pure hydrochloric acid to a liter volume with boiled distilled water. Determine the acid in measured portions of the solution with the standard alcoholic caustic potash, using phenolphthalein as the indicator, and then, without further dilution, proceed to determine the strength of the acid as directed under II.

II. BY MEANS OF CARBONATES

Dissolve about 6.5 grams of potassium hydroxide in a liter of distilled water. The solution will be somewhat more than decinormal. It is not necessary to know its exact strength, nor is it necessary to boil the water with which it is made.

Weigh into beakers or Erlenmeyer flasks two portions of pure calcium carbonate of about 0.2 gram each. Add to each portion 50 cc. of the hydrochloric acid whose strength was determined as directed under I, *d*, and cover the beakers or flasks with watch glasses. When the solution of the carbonate — which may be hastened by the application of a very gentle heat — is complete, rinse the covering glasses into the solutions with distilled water, add a few drops of a dilute solution of methyl orange, and titrate the excess of hydrochloric acid with the water solution of potassium hydroxide. Having found how much of the latter is required to neutralize the former, measure out an equal volume of the alkali and titrate it with the hydrochloric acid whose strength is to be determined. The difference between the volume of the acid required to neutralize

the alkali and that added to the carbonate in the first place is, of course, the volume of the acid which has been neutralized in dissolving the carbonate. From this and from the known weight of the carbonate it is easy to calculate the concentration of the hydrochloric acid. The two results should agree very closely with each other and with those obtained by proceeding as directed under I, *d*.

Dilute the acid to the decinormal standard (using boiled distilled water for the purpose) and compare the diluted solution with the decinormal oxalic acid, using for this purpose the standard alcoholic solution of potassium hydroxide and phenolphthalein. Equal volumes of the two acids should neutralize the same volume of the alkali.

Saturate a small quantity of so-called absolute alcohol with potassium hydroxide, and when the liquid has become clear dilute 10 cc. of the solution to a liter with recently boiled water. With the aid of this solution compare again the two decinormal acids, using at one time phenolphthalein and at another litmus as the indicator.

Calcium carbonate for the standardization of acids may be prepared in the following manner: Calcium chloride, such as is usually employed for drying gases, is dissolved in water; the solution is treated with a little calcium hydroxide, boiled, and filtered; the calcium is then precipitated as oxalate with ammonium oxalate and a little ammonia. After standing in a warm place for several hours the oxalate is collected on a filter, washed with water, dried, and converted into carbonate by heating it in a platinum dish. The carbonate is dissolved in hydrochloric acid and the calcium reprecipitated as oxalate; and from the oxalate the carbonate is obtained in the same manner as before. The carbonate thus obtained will probably have a gray color in consequence of the separation of carbon. It is dissolved in hydrochloric acid and the solution, if not perfectly clear, is filtered. The calcium is now precipitated as carbonate with ammonia and ammonium carbonate. The precipitate is collected,

thoroughly washed with boiling water, dried, transferred to a platinum dish, moistened with a solution of ammonium carbonate, and heated to constant weight at a temperature below a red heat. The treatment with ammonium carbonate and the subsequent heating to constant weight should be repeated until such repetition is found to produce no change in the weight of the material.

The crystallized calcium carbonate known as Iceland spar is often pure enough to be used in determining the strength of acids, but much of the material now sold under that name contains magnesium carbonate. It is therefore unsafe to employ a specimen of the mineral for this purpose until its purity has been demonstrated.

OTHER METHODS OF STANDARDIZING ACIDS AND ALKALIES

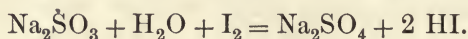
In general, any substance of pronounced acid or basic character which can be obtained in pure condition and is stable in the air may be employed to standardize alkalies and acids.

Of the acids which satisfy these conditions, none are superior to oxalic acid. There are, however, several acid salts which may be used with advantage for the purpose, such as the acid oxalates of the alkali metals and acid potassium tartrate. The compound of this class which is most frequently employed is potassium tetroxalate.

Of the basic substances suitable for the determination of the strength of acids, the carbonates of sodium and of the alkaline earths are probably the best, though certain oxides, e.g. the oxide of zinc, may be used.

The concentration of acids may be determined by precipitating and weighing their insoluble salts, such as barium sulphate, silver chloride, and silver bromide. There are also certain reactions which are attended by the liberation or the consumption of definite quantities of acid, and some of these may be utilized to produce an acid of known strength, or to ascertain the

strength of an acid of unknown concentration. An example of such reactions is furnished by the following equation :



If the quantity of the iodine which takes part in the reaction is known, the quantity of the resulting hydriodic acid can be calculated, and this may be employed to determine the neutralizing power of any solution of an alkali.

A few of the methods of standardizing alkalies and acids will be given in greater detail.

1. *By Means of Potassium Tetroxalate*

Potassium tetroxalate, $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$, may be used with advantage instead of oxalic acid. The salt is stable in the air at ordinary temperatures ; but, like oxalic acid, it cannot be dried in a hot-air bath or in a desiccator. It is best prepared in the following manner: A concentrated solution of oxalic acid is divided into two parts, one of which is slightly less than a fourth of the whole. The smaller portion is heated to the boiling point, treated with a little litmus, and carefully neutralized with pure potassium carbonate. The larger portion is then heated and the solution of potassium oxalate stirred into it. If any tetroxalate separates during the mixing of the liquids, the heating is continued, with addition of more water if necessary, until a clear solution is obtained. The solution is stirred while crystallizing to prevent the formation of large crystals, which are much more apt than the smaller ones to include mother liquor. The product should be recrystallized once or twice from pure distilled water. The crystals are collected in a funnel, in the bottom of which a platinum cone or a perforated porcelain disk has been placed, and freed to the greatest possible extent, with the aid of a filter pump, from mother liquor. Finally, they are washed with a little cold water and dried in the air upon unglazed porcelain plates.

The tetroxalate is a tri-basic acid with a molecular weight of 252.22; a normal solution of it would, therefore, contain in a liter-volume 84.0733 grams of the salt.

2. *By Means of Sodium Carbonate*

The substance which has been longest and probably most frequently employed for the standardization of acids is the neutral anhydrous carbonate of sodium. It is prepared for use either from the acid salt or from the crystallized neutral carbonate by heating in a platinum vessel until everything volatile has been expelled. The product is hygroscopic and must therefore be preserved in closed bottles. The portion of the material which is to be used in any experiment should be reheated in a small platinum crucible or boat, cooled in a desiccator, and protected from the moisture of the air while weighing by inclosing it in a weighing glass. If an indicator is used which, like litmus and phenolphthalein, is sensitive to carbonic acid, the neutralization of the carbonate must take place in a boiling solution.

3. *By Means of Sulphuric Acid derived from Copper Sulphate*

If an aqueous solution of copper sulphate is subjected to electrolysis, it is quantitatively decomposed into metallic copper and free sulphuric acid. It is evident that if the sulphate is pure and the weight of it is known, the quantity of the acid which will be liberated can be calculated; also that this known quantity of acid may be utilized to determine the strength of any alkaline solution, which may in turn be employed to standardize other acids. The sulphate should be purified by repeated crystallizations. It is stable in the air at ordinary temperatures, but cannot be dried in a desiccator or in a hot-air bath. The electrolysis may be effected in a platinum dish with precipitation of the copper upon the platinum, or in a beaker glass with use of any of the ordinary forms of platinum electrodes.

CHAPTER VI

THE DETERMINATION OF SPECIFIC GRAVITY

DENSITY AND SPECIFIC GRAVITY

The terms *density* and *specific gravity*, as they are ordinarily employed, have the same significance, though the former is usually applied to gases and the latter to liquids and solids. Both are used to signify the amount of matter in an object, or its mass, as compared with the mass of an equal volume of some standard substance. If any distinction between the terms is to be attempted, we might define density as the *mass* of a unit volume of any object, and specific gravity as the *weight* of a unit volume of the same; in which case density = $\frac{\text{mass}}{\text{volume}}$, and

specific gravity = $\frac{\text{weight}}{\text{volume}}$. But this distinction is immaterial since in all the practice of the chemist the terms *mass* and *weight* have fundamentally the same significance. In a certain sense the term *specific gravity* is misleading, for it suggests the erroneous idea that the density of an object is in some way dependent on the force of gravity, which is a variable quantity.

Water at 4° C. has been selected as the standard for the comparison of liquids and solids with respect to specific gravity or density. If the cubic centimeter and the gram are employed as the units of volume and mass, the unit of specific gravity and that of weight are in all respects identical, since both are the cubic centimeter of water at 4°. The specific gravity of any liquid or solid may then be defined as the weight in a vacuum of one cubic centimeter of the substance, and conversely, the

specific volume of any liquid or solid may be defined as the volume of one gram of the substance.

Owing to the lightness of gases as compared with other forms of matter and also to the simple relation existing between their weights and those of the molecules of which they are made up, it is more convenient to employ some gas as the standard of density for this class of bodies. Hydrogen is usually made the standard for comparison. Accordingly the density of a gas may be defined as its weight in a vacuum as compared with the weight of an equal volume of hydrogen when measured under the same conditions of temperature and pressure. The molecular weight of any gas may then be found by doubling its density, since hydrogen with a density of 1 has a molecular weight of 2, and the molecular weights of all gases are proportional to their densities.

Air is also employed as a standard for the comparison of gases with respect to density. It is, however, ill adapted to the purpose owing to the variability of its composition.

The density of an object changes with its volume and its volume varies with its temperature. It is therefore necessary to fix upon a standard temperature not only for the standard substance but also for all of those substances which are to be compared with it. As stated already, the standard temperature for water (the standard substance) is 4° , — the temperature of its maximum density. The standard temperature for other substances is 0° . A strict adherence to the latter standard is, however, practicable only in the case of those substances whose cubical expansion coefficients are known. Hence in many instances it is possible only to give the specific gravity of a liquid or solid for the particular temperature at which it was experimentally determined.

The temperature at which all gases are compared with respect to density is 0° . Owing to their compressibility there is required for gaseous bodies a second standard, — that of pressure. The standard pressure is that which will, at 0° , support a vertical

column of mercury 760 mm. in length. But, since the pressure required to support such a column of mercury varies with the intensity of the earth's attraction, it is necessary to define the latitude and altitude at which it shall be valid as a standard. The latitude and altitude agreed upon are 45° and sea level.

EXERCISE XI

DETERMINATION OF THE SPECIFIC GRAVITY OF SOLIDS

I. DETERMINATION OF THE SPECIFIC GRAVITY OF A SILVER COIN

There are required:

1. A thoroughly cleansed silver dollar or half dollar.
2. A fine platinum wire long enough to suspend the coin at the proper distance above the balance pan.
3. A beaker glass of recently boiled distilled water which has cooled to the temperature of the balance room.
4. A bridge to place over the balance pan as a support for the beaker.

Weigh the coin and then suspend it in a loop on the end of the wire at the proper height above the pan. Remove the coin from the loop, leaving the wire in its place on the hook. Place the beaker of water on the bridge over the pan and weigh the wire with the loop submerged in the water. Remove the wire, replace the coin in the loop, suspend it in a beaker of hot water, and then boil until all air is expelled from the surface of the coin. Immerse the coin for a few minutes in cold water, and then transfer it, still wet, to the water on the bridge. Weigh the coin submerged in the water and note the temperature of the latter.

The difference between the last weight and that of the wire with its loop submerged is the weight of the coin in water.

The difference between the weight of the coin in air and in water is the weight of a volume of the water equal to that of the coin.

Correct the weight of the coin and that of the water displaced by it to a vacuum, using 0.0012 gram as the weight of a cubic centimeter of air; 8.4 and 21.5 as the specific gravities of the brass and platinum weights respectively; $\frac{\text{weight of coin}}{\text{weight of displaced water}}$ as a sufficiently close approximation to the specific gravity of the coin; and the proper value, to be found in the tables, as the density of the water.

Divide the corrected weight of the coin by the corrected weight of the water. The quotient is the specific gravity of the former as compared with water at the temperature of the experiment. To find the specific gravity of the coin as compared with water at 4°, the result must be multiplied by the density of the water at the time of weighing the coin in it. An exact determination would also involve a correction for the expansion of the coin from 0° to the temperature of the water at the time of the experiment; but since its expansion coefficient is unknown, this correction cannot be applied.

II. DETERMINATION OF THE SPECIFIC GRAVITY OF GLASS IN FRAGMENTS

There are required:

1. A specific-gravity flask with a perforated stopper (Fig. 20).
2. From 10 to 15 grams of broken glass.

Cleanse the flask first with an alcoholic solution of caustic potash and then with distilled water. Drain it thoroughly and wipe the outside with filter paper. Insert a cork through which have been passed a filled calcium chloride tube and a small glass tube which reaches nearly to the bottom of the flask. Aspirate air through the flask until it is dry. Weigh the flask by the method of Borda or Gauss, — first empty and then with the glass whose specific gravity is to be determined. Cover the glass with distilled water. Place the flask under a bell jar which is connected with an air pump and exhaust until the



FIG. 20

air has been removed from the surface of the glass. Fill the flask with recently boiled distilled water and insert the stopper. Place it in a water bath having a temperature a few degrees above that of the balance room. Stir the water in the bath and keep it for a long time at a constant temperature, still above that of the balance room, by adding water of a higher temperature whenever necessary. Remove the flask from the bath, carefully cleanse the outside with filter paper, and then allow it to stand for an hour or more in the balance case. Weigh by the same method as before.

Remove the broken glass, fill the flask with distilled water, heat in the bath to the same temperature as before, remove the flask, cleanse, cool and weigh it as in the first instance.

Let P represent the weight of the flask,

P , the weight of the flask and the glass,

W the weight of the flask when filled with glass and water, and

W , the weight of the flask when filled with water alone.

Then $P - P$ is the weight of the glass a , and $(P - P) + W - W$ is the weight of the water displaced by the glass b .

Reduce a and b to their weights in a vacuum, using $\frac{a}{b}$ as the specific gravity of the glass, and divide the corrected value of a by the corrected value of b . The quotient will be the density of the glass as compared with that of water when both have the temperature of the bath. We wish, however, to compare glass at 0° with water at 4° . For the purpose of explaining the method of applying the temperature corrections, we will assume that the temperature of the bath was 25° and let a and b represent the corrected weights of the glass and of the displaced water. The commonly accepted cubical-expansion coefficient of glass is 0.000025. Accordingly a unit volume of glass at 0° becomes 1.000625 volumes at 25° . A unit volume of water at 4° becomes 1.002868 volumes at 25° . Now if we suppose the volumes of the glass and of the water to be kept constant by the addition of more material while the temperature of the

former falls from 25° to 0° , and that of the latter from 25° to 4° , the final weight of the glass will be $a, \times 1.000625$ grams, and that of the water displaced will be $b, \times 1.002868$ grams. Hence the specific gravity of the glass at 0° as compared with water at 4° will be $\frac{a}{b} \times \frac{1.000625}{1.002868}$.

The student should familiarize himself with the use of Jolly's balance and of Nicholson's hydrometer for the determination of the specific gravity of solids.

He should also work out in detail:

1. A method for determining, by weighing in water, the specific gravity of a substance which is lighter than water.
2. A method for determining, by weighing in benzene (sp. gr. 0.88), the specific gravity of a substance which is soluble in water.
3. A method of determining the specific gravity of a substance by measuring the water, or other liquid, which it displaces.

EXERCISE XII

DETERMINATION OF THE SPECIFIC GRAVITY OF LIQUIDS

I. WITH THE PYCNOMETER

There are required:

1. An Ostwald (Fig. 21) or Sprengel (Fig. 22) pycnometer.
2. A quantity of pure benzene.

Wet the outside of the instrument with distilled water and then dry it with filter paper. Suspend it by a platinum wire from the hook over the balance pan, and weigh. Attach to b a rubber tube, which is in turn connected with a full pipette, —or with any other arrangement to prevent the entrance of saliva into the rubber tube, —and immerse the end a in recently boiled distilled water

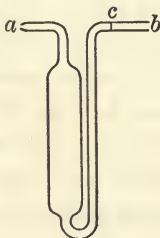


FIG. 21

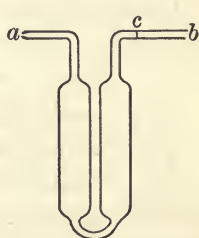


FIG. 22

which has cooled to the temperature of the room. Fill the apparatus by moderately diminishing the pressure within and

suspend it by the platinum wire in a bath of distilled water having a temperature slightly above that of the air. Maintain the bath for a considerable time at a constant temperature as directed in Exercise XI under II. Just before removing the instrument from the bath, touch the point *a* with filter paper until the liquid in the tube recedes to the mark *c*. If, by accident, too much liquid is withdrawn, the difficulty may be remedied by touching the end of the tube *a* with a drop of water on a glass rod. Remove the pycnometer from the bath, dry it with filter paper, and weigh when its temperature has fallen to that of the balance room. Empty the pycnometer, rinse with successive small portions of strong alcohol, then with ether which leaves no residue on evaporation, and dry by aspirating air through it.

Fill the apparatus with benzene and proceed in exactly the same manner as when it was filled with water, being very careful to maintain the bath at the same temperature as before.

Having found the relative weights (reduced to a vacuum) of equal volumes of water and benzene at the temperature of the bath, calculate the specific gravity of the latter at 0° as compared with the former at 4° , using 0.00138 as the cubical expansion coefficient of benzene.

II. BY WEIGHING AN OBJECT IN TWO LIQUIDS

Construct a glass sinker, Fig. 23, with a little mercury in the bottom to increase its weight and to keep it in a vertical position when submerged in a liquid. The instrument should have a volume of from 10 to 15 cc. Place in the balance case two well-covered cylinders, one containing distilled water and the other pure benzene. Suspend



FIG. 23

the sinker by a platinum wire from the stirrup hook and weigh it, first in the air, next in the water, and finally in the hydrocarbon, taking care that the same length of wire is submerged in both liquids. Note the temperature of the water and of the benzene, which, of course, should be the same.

Let W represent the weight of the sinker in air,

W_w its weight in water,

W_b its weight in benzene.

Then $W - W_w$ is the weight of the water displaced by the sinker, and

$W - W_b$ is the weight of an equal volume of benzene.

Reduce the weights to their values in a vacuum and find the density of benzene at 0° as compared with that of water at 4° .

III. BY THE MOHR-WESTPHAL BALANCE

The principle employed in the preceding experiment is utilized in a convenient manner in the construction of the Mohr-Westphal balance, Fig. 24. There are several modifications of the instrument, but in its usual form it consists essentially of a beam without pans. One arm is shorter and heavier than the other and serves only as a counterpoise. The longer and lighter arm is graduated into ten equal divisions. At the end of the graduated arm is suspended by a platinum wire a thermometer which serves as a sinker. The adjustment is such that the balance is in equilibrium when the sinker is suspended in air.

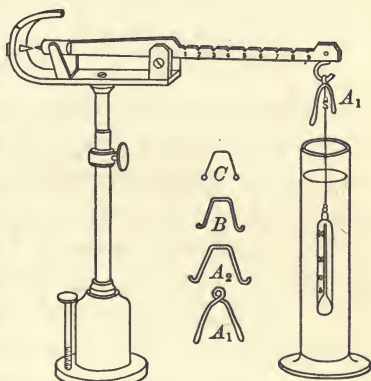


FIG. 24

The weights are of three or four denominations in decimal order. The heaviest one is just equal to the loss in weight which the sinker suffers when it is immersed in water having a temperature of 15° . Hence if the sinker is submerged in water of that temperature and one of the heaviest weights is placed upon the hook from which the sinker is suspended, the balance will again be in equilibrium.

To determine at the same temperature the specific gravity of a liquid heavier than water, one of the heaviest weights is placed upon the hook, the sinker is immersed in the liquid, and other weights are then distributed along the arm until equilibrium is obtained. Suppose we represent the weights in their descending order by A_1 , A_2 , B , and C , and that in a given experiment the distribution along the arm, when the balance is in equilibrium, is as follows: A_1 on the 10th division (i.e. on the hook), A_1 on the 5th, A_2 on the 3d, and B on the 9th. The specific gravity of the liquid is 1.539.

When the specific gravity of a liquid lighter than water is to be determined, the weight A_1 is removed from the hook. Care must be taken that the depth to which the platinum wire is submerged in the different liquids is always the same.

HYDROMETERS (AREOMETERS, DENSIMETERS)

Instruments of this kind are constructed in accordance with the principle that a body will sink in a liquid which is specifically lighter than itself until it has displaced its own weight of the liquid.

There are two classes of hydrometers. In one of these the immersion of the instrument is constant, and in the other variable. As examples of the first class, we have the hydrometers of Fahrenheit and of Nicholson; and of the second, the volumeter of Gay-Lussac, the ordinary specific-gravity spindles, the hydrometers of Beaumé and of Twaddell, alcoholometers, etc.

Of these two classes of hydrometers, examples of which are described in the following pages under *A* and *B*, only instruments of the second variety, i.e. those of variable immersion, are employed by the chemist. Instruments belonging to the first class, i.e. those of constant immersion, are, however, of interest to him from the standpoint of the principles which are involved in their construction.

CLASS A

Instruments of Constant Immersion

1. FAHRENHEIT'S HYDROMETER

This instrument, Fig. 25, is made wholly of glass. It consists (1) of a small bulb a , which is filled with mercury to keep the apparatus in a vertical position when swimming in a liquid; (2) of a larger bulb b , which gives to the instrument the necessary volume; (3) a narrow tube c , on which is made a mark showing to what depth the instrument is to be immersed; (4) a cuplike enlargement of the tube d , which serves as a receptacle for the weights by which the requisite degree of submersion is effected.



FIG. 25

If the hydrometer is placed in water of any required temperature, e.g. 15° , and weights are added to the cup until the instrument sinks in the liquid to the mark on the stem, it is clear that the weight of the water displaced will be equal to the sum of the weights of the instrument and of the load placed in the cup.

Let W represent the weight of the displaced water,

P the weight of the instrument (previously ascertained),
and

P_1 the sum of the weights in the cup.

Then $W = P + P_1$.

Suppose the hydrometer to be placed in any other liquid of the same temperature, and to be sunk to the mark by the addition of the required weights. The volume of the liquid displaced will be the same as before.

Let W_1 represent the weight of the displaced liquid,

P_1 the sum of the weights in the cup.

Then $W_1 = P + P_1$, and the specific gravity of the liquid for the given temperature, as compared with that of water at the same temperature, is $\frac{W_1}{W}$.

2. NICHOLSON'S HYDROMETER,

Nicholson's hydrometer, Fig. 26, differs from Fahrenheit's in that it is usually made of metal, and has suspended from its lower end a basket or bucket in which a solid substance may be weighed under a liquid. It is chiefly used for the determination of the specific gravity of solids. Its weight is so adjusted that a fixed additional weight, e.g. 100 grams, is required to sink the instrument to the mark in water of standard temperature, e.g. 15° . To determine the specific gravity of a solid, the substance is placed in the cup and weights are added until the hydrometer sinks to the mark in water of standard temperature. The object is then transferred to the basket below and more weights are added until the hydrometer sinks to the same point as before.



FIG. 26

Let P represent the fixed weight,

P_1 weights added when the substance was in the cup,

P_{II} the sum of the weights in the cup when the substance was in the basket,

W the weight of the substance in the air, and

W_1 the weight of the water displaced by the substance.

Then $W = P - P_1$, $W_1 = P_{II} - P_1$, and the specific gravity of the object is $\frac{W}{W_1}$.

CLASS B

Instruments of Variable Immersion

1. GAY-LUSSAC'S VOLUMETER

The hydrometer of Gay-Lussac is called a volumeter because the principle employed in its construction is such that one reads upon its scale the volume of that portion of the instrument which is immersed in a liquid. The glass tube represented in

Fig. 27 is supposed to be of uniform diameter throughout, to be closed at the lower end, and to be graduated upward from 0 to 200 in divisions of equal length. If such a tube is placed in water of any standard temperature and weighted with mercury until it sinks to the 100 mark and is then transferred to a heavier liquid of the same temperature in which it sinks to the 80 mark, it is clear that 80 volumes of the heavier liquid have the same weight as 100 volumes of the water; also that the specific gravity of the former is $\frac{100}{80}$, or 1.25, since the densities of different substances are inversely proportional to the volumes of equal weights.

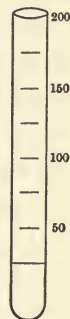


FIG. 27

An instrument of the form represented in Fig. 27 would not be sufficiently sensitive owing to the great width of the tube bearing the scale. The Gay-Lussac hydrometer is therefore usually made in the form represented in Fig. 28.



FIG. 28

For the purpose of effecting its graduation, the instrument is placed first in water of the standard temperature and then in sulphuric acid of the same temperature which has a specific gravity of 1.25. The points to which it sinks in the two liquids are designated by the numbers 100 and 80 respectively. The space between these two fixed points is graduated into 20 equal parts, and the graduation is then continued uniformly up and down the tube. The specific gravity of any liquid will be found by dividing 100 by the number of volumes immersed, as read upon the scale of the instrument.

The volumeter may also be graduated without the aid of a second liquid of known specific gravity. The method is as follows: The instrument is weighted with mercury until it sinks in water to the point where it is desired to place the 100 mark; its total weight is then exactly doubled by the introduction of more mercury, and the point to which it sinks is designated by the number 200. The space

between the 100 and the 200 marks is divided into 100 equal parts, and the graduation is continued uniformly down the tube as far as may be desired. Instead of doubling the weight of the instrument for the purpose of establishing a second point in the scale, its weight may be reduced to one-half by removing mercury. The point to which the volumeter then sinks in water would be designated by 50.

The hydrometers of Balling and of Brix are constructed on the same principle as the volumeter of Gay-Lussac, the only difference between them and the latter being in the magnitude of the "degree." In the instrument of Balling the point to which the hydrometer sinks in water is designated by 200, and in that of Brix by 400. A degree Gay-Lussac is therefore equal to 2 degrees Balling and 4 degrees Brix.

2. SPECIFIC-GRAVITY HYDROMETERS

Certain hydrometers of variable immersion are graduated by placing the instruments in two or more liquids of different known densities, and then dividing the spaces between the points thus established, also the spaces above and below them,



FIG. 29

into equal divisions whose length bears the proper relation to the differences between the specific gravities of the liquids. That such instruments do not in reality record the densities of liquids except at the points experimentally established will appear from the following consideration. Suppose we have six different liquids whose densities are related as the whole numbers from 1 to 6; also that we have a glass tube, Fig. 29, of uniform diameter, closed at both ends, and of such weight and volume that it will sink in liquid No. 1 until its upper end is on a level with the surface. Let the whole length of the tube be represented by 60. If the tube is placed in liquids Nos. 2, 3, 4, 5, and 6 in succession, the points marked 30, 20, 15, 12, and 10 will, each in turn, coincide with the upper surface of a

liquid; for, according to the law that a body will sink in a liquid until it has displaced its own weight, one-half of the tube will be submerged in liquid No. 2, one-third in No. 3, one fourth in No. 4, one-fifth in No. 5, and one-sixth in No. 6. In other words, while the densities of the liquids are related to each other as 1, 2, 3, 4, etc., the volumes immersed are related as the reciprocals of these numbers. Accordingly, it will be noticed on the graduation of specific-gravity hydrometers that the divisions corresponding to equal differences of density diminish in length in a downward direction. Such instruments are said to be *harmonically graduated*.

3. BEAUME'S HYDROMETER

This instrument is much used in commercial transactions both on the continent of Europe and in America. It consists of two spindles, one for liquids lighter and another for liquids heavier than water. A spindle which is to be graduated for liquids lighter than water is placed in a 10 per cent solution of sodium chloride. The point to which it sinks is designated by 0. It is then transferred to water and the point to which it sinks in this liquid is designated by 10. The space between these two points is divided into ten equal parts, and the graduation is continued uniformly up the stem. A spindle which is to be graduated for liquids heavier than water is placed first in water and then in a 10 per cent solution of sodium chloride (sp. gr. $\frac{15^\circ}{15^\circ} = 1.07335$). The points thus established are designated by 0 and 10 respectively. The space between them is divided into ten equal parts, and the graduation is continued uniformly down the stem.

It will be seen that the so-called degrees Beaumé stand in no very simple relation to the specific gravities of liquids. Expressed in density, the degree 66 on the instrument for heavy liquids has somewhat over three times the value of

degree 1. Considerable confusion has arisen from the negligence of the early makers both in determining and in stating the exact temperature and density of the liquids which they employed in graduating the instruments. The earlier hydrometers were graduated for 12.5° , 15° , and 17.5° . At present, there is in use for liquids heavier than water a Beaumé hydrometer with a so-called "rational scale." This is graduated by placing the spindle first in water at 15° and then in sulphuric acid of specific gravity 1.842 ($d \frac{15^\circ}{15^\circ} = 1.842$). The points to which it sinks are designated by 0 and 66 respectively, and the space between them is divided into 66 equal parts.

The following formulas have been worked out for finding the specific gravity corresponding to any degree Beaumé. The letter n signifies the number of the degree Beaumé, and t the temperature for which the instrument is graduated.

Instruments for Liquids Lighter than Water

$$t = 12.5^\circ, \quad d = \frac{145.88}{135.88 + n}.$$

$$t = 15^\circ, \quad d = \frac{146.3}{136.3 + n}.$$

$$t = 17.5^\circ, \quad d = \frac{146.78}{136.78 + n}.$$

Instruments for Liquids Heavier than Water

$$t = 12.5^\circ, \quad d = \frac{145.88}{145.88 - n}.$$

$$t = 15^\circ, \quad d = \frac{146.3}{146.3 - n}.$$

$$t = 17.5^\circ, \quad d = \frac{146.78}{146.78 - n}.$$

Instrument with "Rational Scale"

$$t = 15^{\circ}, \quad d = \frac{144.3}{144.3 - n}.$$

The "Dutch hydrometer" is the older Beaumé. It is graduated for 12.5° , and the 10 per cent salt solution employed in its graduation is assumed to have a specific gravity of 1.074626 ($d \frac{15^{\circ}}{15^{\circ}}$). The formulas for finding the corresponding specific gravities are

$$d = \frac{144}{134 + n} \text{ for liquids lighter than water, and}$$

$$d = \frac{144}{144 - n} \text{ for liquids heavier than water.}$$

4. BECK'S HYDROMETER

This instrument is graduated by placing the spindle in water and then in a liquid having a specific gravity of 0.85 ($d \frac{12.5^{\circ}}{12.5^{\circ}}$).

The points to which it sinks are designated by 0 and 30 respectively. The space between them is divided into 30 equal parts, and the graduation is continued uniformly both up and down the stem. The standard temperature is 12.5° . The formulas for finding the specific gravity corresponding to any degree Beck are

$$d = \frac{170}{170 + n} \text{ for liquids lighter than water, and}$$

$$d = \frac{170}{170 - n} \text{ for liquids heavier than water.}$$

5. TWADDELL'S HYDROMETER

Twaddell's hydrometer, which is much used in England, is designed for liquids heavier than water. The interval between the points to which it sinks in water and in a liquid twice as

heavy is harmonically divided into 200 spaces or degrees, so that successive divisions on the scale correspond to an increase or decrease of 0.005 in specific gravity. Hence the specific gravity corresponding to any degree Twaddell may be found by multiplying the number of degrees by 0.005 and adding the product to 1.000. Thus a liquid having a density of 10 degrees Twaddell has a specific gravity of $10 \times 0.005 + 1.000$, or 1.05. The Twaddell instrument usually consists of five separate spindles.

6. THE ALCOHOLOMETER

There are also in use a number of special hydrometers, i.e. instruments which serve to determine the concentration, and consequently the commercial value, of individual solutions. The most generally useful of these is the alcoholometer. There are two kinds of alcoholometers. One gives the percentage of alcohol in an aqueous solution by *volume*, and the other by *weight*. The latter kind is but little used, either in the revenue service or in commercial transactions. Alcoholometers are graduated for a particular temperature which is designated upon the instruments. But each instrument is accompanied by a table in which are to be found the necessary corrections when the solutions have other than the standard temperature.

7. THE LACTOMETER

The lactometer is a very sensitive specific-gravity spindle with a scale ranging from perhaps 1.01 to 1.04. The commonest form of the instrument is the "lactodensimeter" of Quevenne, which is employed to detect and to estimate approximately the falsification of milk, either by diluting with water or by skimming. The specific gravity of normal milk ranges from 1.026 to 1.032. If any considerable portion of the butter is removed, the density of the milk becomes too great; while if much water is added, it falls below the normal limit.

The scale of the lactodensimeter ranges from 1.014 to 1.042, and the readings are grouped together by a series of braces placed to the right. The first of these includes the probable range of density of pure milk; the second, that of milk diluted with one-tenth of its volume of water; etc. In some countries there is also legalized, under proper representations as to its character, the sale of so-called "half-skimmed" milk. This milk is also required to come up to certain standards as to percentage of butter and other nutritious constituents. There is therefore placed to the left of the Quevenne scale a second grouping of readings which serves to detect excessive skimming or dilution with water.

SPECIFIC-GRAVITY BULBS

These are hollow glass bulbs on each of which is recorded the specific gravity of a liquid in which it will neither sink nor rise. They are made by blowing bulbs on the end of a glass tube. The bulbs are first roughly assorted by throwing them into liquids of different specific gravities and afterwards they are accurately adjusted by grinding.

DETERMINATION OF SPECIFIC GRAVITY BY DILUTION

The specific gravity of a solid may be determined by placing it in a liquid more dense than itself and then diluting with a lighter liquid until the body will neither float nor sink. At this stage the solid and the liquid are of the same density, and the specific gravity of the former may be ascertained by determining that of the latter by any of the methods applicable to liquids. This procedure is resorted to with advantage when the quantity of available material is too small to admit of an accurate determination of its specific gravity by other methods.

Saturated solutions of the double iodide of potassium and mercury (sp. gr. 3.196), of cadmium borotungstate (sp. gr. 3.36), and of the double iodide of barium and mercury (sp. gr. 3.588),

also methylene iodide (sp. gr. 3.324), are employed in this manner, not only for the determination of specific gravity, but also for the separation of minerals in rock mixtures. The double iodide of potassium and mercury (Thoulet's solution) and the borotungstate of cadmium (Klein's solution) may be diluted with water, but not the double iodide of barium and mercury (Rohrbach's solution), which deposits mercuric iodide when water is added. Methylene iodide (Braun's liquid) may be diluted with benzene or with toluene. The last liquid, methylene iodide, is used for the determination of the specific gravity and the separation of substances which are soluble in water.

THE DENSITY OF GASES

The exact determination of the relative densities of the different gases is one of the most important and at the same time the most difficult of all quantitative chemical problems. The problem is more difficult in the case of gases than in that of liquids and solids, because of the greater number, magnitude, and complexity of the sources of error. Some of the obstacles to a satisfactory solution of it will be mentioned.

Owing to its universal presence as a constituent of the air, and the difficulty of removing it by absorption, it is not easy to obtain any gas which is wholly free from nitrogen.

The prevalence of water vapor and the difficulty of wholly removing it from gases is another source of embarrassment.

The rapid diffusion of gases is always a source of danger to their purity. It makes their isolation difficult, and renders the complete displacement of one gas by another impracticable except through the intervention of the vacuum pump with its complex manipulation.

The great influence of temperature and pressure upon the densities of gases makes necessary exceptional precautions in the determination of the temperature and pressure under which they are measured; while the variability of the standard for

pressure and the lack of a rigid obedience on the part of gases to the laws of Boyle and of Gay-Lussac are a source of some uncertainty in the calculations which are based on such determinations.

Finally, the accuracy of the results is diminished by the fact that it is impossible to operate with more than very small weights of gases and that even these must be weighed in containing vessels which are many times heavier than the gases themselves.

The densities of those gases which were formerly designated as the *permanent gases* have been determined in various ways. Of the methods employed the following are the more important.

1. BY WEIGHING THE GASES DIRECTLY

To determine the density of gases by weighing, two large balloon flasks of equal volume and weight, and provided with gas-tight stopcocks, are suspended from the arms of a sensitive balance. One of them is closed and serves only as a counterpoise, while the other is used as the containing vessel for the gases to be weighed. The weight of the latter is found by weighing the exhausted vessel, and its capacity by weighing the water which is required to fill it. It is then filled with the gas under investigation and again weighed. The use of a counterpoise of the same material and volume as the containing vessel is important not only as a correction for air displacement but also as a means of counteracting the errors in weighing which arise from the variable condensation of atmospheric moisture on the surface of bodies.

Lord Rayleigh has recently pointed out that this method (which was employed by Regnault and afterwards by many others) has in it a source of error hitherto unsuspected, namely, the shrinkage of the containing vessel when it is exhausted for the purpose of determining its weight. The result of such a shrinkage would be, of course, an incorrect

determination of the weight, first of the vessel and ultimately of the gases themselves. J. M. Crafts has determined experimentally the probable amount of this contraction in the vessel used by Regnault, and therefore the correction which is to be applied to Regnault's results. He employed for the purpose not the vessel which Regnault had used, for that had been destroyed, but one similar in all respects, which had been made at the same factory and at the same time. The shrinkage was found by Crafts to amount to 0.000247 of the volume of the vessel.

The following table contains the corrected results of Regnault for the latitude of Paris.

	DENSITY (Air = 1)	DENSITY (Hydrogen = 1)	WEIGHT OF 1 LITER (at Paris)
Air	1.00000	14.391	1.29349 grms.
Nitrogen	0.97138	13.979	1.25647 "
Hydrogen	0.06949	1.000	0.08988 "
Oxygen	1.10562	15.910	1.43011 "
Carbon Dioxide	1.52897	22.003	1.97772 "

2. BY WEIGHING THE GASES AFTER ABSORPTION

This method was first employed by R. F. Marchand. A large glass vessel was filled at 0° and under a constant pressure (765 mm.) with a pure gas. The gas was then forced, by the introduction of a neutral gas, through a weighed tube containing the appropriate absorbent. The increase in the weight of the tube gave the weight of the gas. In this way Marchand determined the relative densities of

Oxygen, which was displaced by carbon dioxide and absorbed by red-hot copper ;

Carbon dioxide, which was displaced by air and absorbed by potassium hydroxide ;

Carbon monoxide, which was burned by copper oxide and the resulting carbon dioxide absorbed in potassium hydroxide ;

Sulphur dioxide, which was displaced by hydrogen and absorbed by potassium hydroxide.

Since by this method the vessel is always filled under the same conditions, the volumes of the several gases are equal and the weights found are therefore strictly proportional to their densities. It will be seen that it is not necessary to know the capacity of the vessel unless in addition to their relative densities it is desired to ascertain the weights of a unit volume of the gases.

In one respect the method of Marchand is superior to that of Regnault. It does away with the necessity of weighing the containing vessel, which is the most critical step in the Regnault procedure.

A similar method was employed by J. P. Cooke to ascertain the weight of the containing vessel which he used in his determination of the atomic weight of oxygen. The vessel was filled with carbon dioxide and weighed. The gas was then absorbed and weighed. The difference between the two weights was the weight of the vessel.

It will be seen that the displacement and absorption method may also be used to determine the capacity of a vessel, or an apparatus, such, for instance, as an air pump.

3. BY THE TIME REQUIRED FOR DIFFUSION

It was shown by Graham that, under the same conditions of temperature and pressure, the times required for the diffusion through a small aperture of equal volumes of different gases are inversely proportional to the square roots of the densities of the gases. Bunsen (see *Gasometrische Methoden*, 2. Auflage, page 184) has founded upon this principle a simple method for the determination of the relative densities of gases. The method is not more accurate than that of Regnault or of Marchand, but has the advantage of requiring only small volumes of the gases.

CHAPTER VII

THE DETERMINATION OF MOLECULAR WEIGHTS

ATOMIC RATIOS

The following examples are given to illustrate the method by which one finds, from the results of a quantitative analysis of any compound, the atomic ratios of the constituents.

1. COPPER OXIDE

Suppose by reducing a known weight of cupric oxide in a current of hydrogen and weighing the resulting metallic copper, it is found that the compound contains 79.8 per cent of copper and 20.1 per cent of oxygen. If we divide the first quantity by 63.1, the atomic weight of copper, and the second by 15.88, the atomic weight of oxygen, we shall obtain the numbers 1.264 and 1.265, which are related to each other as are the numbers of the atoms of the two elements in the compound. If we divide the numbers representing the atomic ratios by the smaller of the two (1.264), with a view to reducing them to whole numbers without disturbing their ratio, we shall obtain 1 and 1.00079. The second number is so nearly unity that we may fairly assume that the excess, 0.00079, originated in the unavoidable errors of analysis or is due to a slight inaccuracy in the number representing the atomic weight of copper. If so, there are as many atoms of copper as of oxygen in a molecule of copper oxide, and the simplest formula which we can assign to the compound is CuO .

2. POTASSIUM PERMANGANATE

An analysis of this compound shows it to consist, approximately, of potassium 24.7 per cent, manganese 34.8 per cent, and oxygen 40.5 per cent. By dividing the percentage of each constituent by its atomic weight and reducing the ratio to one of whole numbers, we find that $K : Mn : O :: 1 : 1 : 4$. That is, there are in the compound as many atoms of potassium as of manganese and four times as many atoms of oxygen as of either potassium or manganese. The simplest possible formula for the compound is therefore $KMnO_4$.

3. ACETIC ACID

Acetic acid contains very nearly 40 per cent of carbon, 53.3 per cent of oxygen, and 6.7 per cent of hydrogen. Hence $C : O : H :: 3.361 : 3.356 : 6.700 :: 1.001 : 1 : 1.996$. The slight variations from whole numbers are probably due to errors of analysis and the slight inaccuracies of the numbers assumed to represent the atomic weights of carbon and hydrogen. We must therefore conclude that acetic acid contains as many atoms of carbon as of oxygen and twice as many atoms of hydrogen as of either carbon or oxygen. The simplest formula which the compound can have is CH_2O .

4. PROPYL-AMINE

This compound contains 63 per cent of carbon, 23.75 per cent of nitrogen, and 15.25 per cent of hydrogen. Proceeding as before, we find that

$C : H : N :: 5.294 : 15.25 : 1.7049 :: 3.105 : 8.989 : 1 :: 3 : 9 : 1$.
As determined by analysis, the formula of the compound is therefore C_3H_9N .

5. BENZENE

Benzene contains about 92.3 per cent of carbon and 7.7 per cent of hydrogen. Dividing these numbers by 11.9 and 1 respectively, we obtain 7.756 and 7.7. Hence $C:H :: 7.756:7.7 :: 1:1$, and the simplest formula which can be assigned to the compound is CH .

In the examples previously given it has been necessary, in order to find the atomic ratios of the constituents of a compound, only to divide the percentage of each element by its atomic weight and then to divide all of the quotients by the smallest one among them. The results were in all cases so nearly whole numbers that the fractions could reasonably be ascribed to errors of analysis or to the use of slightly incorrect values for the atomic weights of the elements. These fractions are, however, often too large to be accounted for in this manner. In such cases it is clear that the ratios must be multiplied by numbers which will convert the fractions into whole numbers. To illustrate this, we will consider the case of toluene. The compound is shown by analysis to contain 91.3 per cent of carbon and 8.7 per cent of hydrogen. Proceeding as before, we find that $C:H :: 7.672:8.7 :: 1:1.1339$. The fraction 0.1339 amounts to 11.8 per cent, or about one-eighth of the whole hydrogen. That an error of this magnitude could have been made in the analysis is improbable. We must therefore conclude that $C:H :: 1 \times 7:1.1339 \times 7 :: 7:7.9373 :: 7:8$, and that the simplest formula which toluene can have is C_7H_8 .

The determination of atomic ratios in compounds of high molecular weights is somewhat uncertain owing to the considerable effect, in such cases, of small errors of analysis. Suppose a certain hydrocarbon to contain, theoretically, 85.05 per cent of carbon and 14.95 per cent of hydrogen. Using 11.9 and 1 as the atomic weights of the elements, we should find that

$$C:H :: 7.14706:14.95 :: 1:2.091825 :: 10:20.92.$$

Regarding the fraction 0.92 as due to the fact that the calculation of the percentages of the constituents is correct only to the

second decimal place, we should conclude that the atomic ratio of the elements is expressed by the formula $C_{10}H_{21}$. Suppose, however, on analyzing the compound for the purpose of determining the ratio, we obtained 84.85 per cent of carbon and 15.15 per cent of hydrogen, i.e. 0.2 per cent too little of the former and 0.2 per cent too much of the latter. We should then find that $C : H :: 7.13025 : 15.15 :: 1 : 2.12475 :: 7 : 14.873 :: 7 : 15$, and assign to the compound the formula C_7H_{15} .

We are able, by means of the foregoing process, to ascertain the relative but not the absolute numbers of the different kinds of atoms in a compound molecule. It is possible, for instance, to determine by analysis that in a molecule of acetic acid $C : H : O :: 1 : 2 : 1$. It does not follow, however, that the formula of the compound is CH_2O . It may be $C_2H_4O_2$, $C_3H_6O_3$, or any other multiple of the ratio $C_1 : H_2 : O_1$. To decide which of these possible formulas is the correct one, the chemical analysis must be supplemented by a determination of the molecular weight of the substance.

MOLECULAR WEIGHTS

The methods by which molecular weights are determined are usually classified as *chemical* and *physical*.

THE CHEMICAL METHOD

The chemical method of determining molecular weights cannot be concisely defined. It consists, in general, of a study of the reactions of the substances, both those which can be followed quantitatively and those which throw light upon the character of the groupings of the atoms within the molecules. If it can be shown, for example, that a given compound contains two hydroxyl groups, or one hydroxyl and one carbonyl group, it is certain that the compound contains not less than two atoms of oxygen. Again, if its hydrogen can be replaced by another

univalent element or group in four different but equal portions, it is certain that the compound contains four, or some multiple of four, atoms of hydrogen. And if never less than one-fourth of the hydrogen is replaced at any one time, it is probable that the compound contains exactly four, and not some multiple of four, atoms of hydrogen. Many formulas, otherwise plausible, may be discarded for the simple reason that they are inconsistent with the known valence of the constituents; e.g. the formula CH for benzene would be rejected because it represents carbon and hydrogen as of equal valence.

The usefulness and some of the limitations of the chemical method will be illustrated by applying it to the compounds already cited.

The atomic ratio of copper and oxygen in cupric oxide was found by analysis to be as 1 : 1. The simplest possible formula of the substance is therefore CuO . There is no reason for rejecting this formula as inconsistent with what is believed to be the valence of the constituents, nor is any evidence of a more complicated composition to be found in any of its reactions. We therefore accept the formula CuO as probably correct.

In the case of potassium permanganate the chemical evidence is nearly as negative as in that of copper oxide. In fact, very little evidence can be obtained from the reactions of the compound, either as to the relations of the atoms within the molecule or as to their absolute number. It is therefore impossible to decide by means of the chemical method whether the formula of the compound is KMnO_4 , $\text{K}_2\text{Mn}_2\text{O}_8$, $\text{K}_3\text{Mn}_3\text{O}_{12}$, or some other multiple of $\text{K}_1\text{Mn}_1\text{O}_4$.

The method may, however, be applied to acetic acid with more satisfactory results. It is shown by analysis that in this compound $\text{C} : \text{H} : \text{O} :: 1 : 2 : 1$, and the simple formula CH_2O is in accord with the supposed quadrivalence of carbon, the bivalence of oxygen, and the univalence of hydrogen. But a study of the reactions of the substance brings to light many reasons for assigning to it the formula $\text{C}_2\text{H}_4\text{O}_2$. Two of these will be

given. There is, on the whole, good reason for regarding acetic acid as mono-basic, but when its salts with metals are examined they are found still to contain three-fourths of the hydrogen of the acid, proving the presence of 4 atoms of hydrogen in the acid. Again, one, two, and three fourths of the hydrogen of the acid may be successively replaced by one, two, and three equivalents of chlorine. The molecular weights of acids may be determined by an analysis of their salts. As already stated, acetic acid is regarded as mono-basic. If this view is correct, its salts are formed by the replacement of a single atom of hydrogen in each molecule of the acid by a metal or its equivalent, and its salts containing univalent metals consist of one acid residue (a molecule of the acid less one atom of hydrogen) and a single atom of metal. Evidently a determination of the quantity of metal which is contained in a known weight of any such salt will enable us to ascertain the molecular weight of the acid. The silver salts of acids are usually employed in such determinations of molecular weights. They are easily obtained in pure condition, and their analysis is exceedingly simple. If a weighed quantity of silver acetate is ignited in a crucible, the acid residue is volatilized and there remains in the crucible nothing but the silver. On weighing this it is found that the salt consists of very nearly 64.67 per cent of silver and 35.33 per cent of volatile matter. Hence $64.67 : 35.33 :: 107.11 :$ the molecular weight of the acid residue. The proportion gives us 58.51 as the weight of the acid which was in combination with 107.11 parts (one atom) of silver. If we add to this 1 for the atom of hydrogen which was displaced by the silver, we shall obtain 59.51 as the molecular weight of acetic acid, which corresponds to the formula $C_2H_4O_2$ ($23.8 + 4 + 31.76 = 59.56$). This method of determining molecular weights is applicable to all mono-basic acids. It may also be applied to poly-basic acids provided it is known with sufficient certainty what proportion of the acid hydrogen has been replaced in forming the salts which are analyzed.

The molecular weights of many organic bases may be determined by a method as simple as that which is employed for the acids. These bodies are to be regarded as substituted ammonias, and, like ammonia, they form well-defined double salts when treated with platinum chloride and hydrochloric acid. Such salts are decomposed, when heated, with volatilization of everything except the platinum. If a weighed quantity of the double chloride of propyl-amine and platinum is heated in a crucible, the salt is found to consist of 37 per cent of platinum and 63 per cent of volatile matter. Hence $37 : 63 :: 193.4$ (at. wt. Pt.) : molecular weight of the volatile matter. The proportion gives 329.3 as the weight of all the matter which was in combination with 193.4 parts, or one atom, of platinum. The molecular weight of the double salt is therefore $193.4 + 329.3$, or 522.7. We may regard a molecule of the double chloride of ammonium and platinum as made up of two molecules of ammonia, two of hydrochloric acid, and one molecule of platinum chloride; thus $(\text{NH}_3)_2 (\text{HCl})_2 \text{PtCl}_4$. The corresponding double salt of propyl-amine would then be $(\text{propyl-amine})_2 (\text{HCl})_2 \text{PtCl}_4$; and if we subtract from 522.7 (the molecular weight of the compound, 406.48) the molecular weight of $(\text{HCl})_2 \text{PtCl}_4$, the difference, 116.22, will be the weight of the two molecules of the base. The molecular weight of propyl-amine is therefore 58.63, and its formula is $\text{C}_3\text{H}_9\text{N}$ ($35.7 + 9 + 13.93 = 58.63$).

This method suffices for the determination of the molecular weights of all mono-acid bases, i.e. for any base a molecule of which is derived by substitution from a single molecule of ammonia. It may also be applied to those poly-acid bases whose acid equivalence is known. The molecular weights of basic substances may be ascertained with equal certainty by determining how much of them is required to neutralize known quantities of acids. In this case, also, the acid-equivalence of the base, i.e. the number of molecules of a mono-basic acid it can neutralize, must be known.

Benzene will serve to illustrate the application of the chemical method of determining molecular weights to substances which are neither acids nor bases. An analysis shows that in it $C:H :: 1:1$. The simplest formula which the compound can have is, therefore, CH . It is found, however, on treating benzene with chlorine that the hydrogen in it is replaced in several different stages, and that in the compound containing the least chlorine only one sixth of the hydrogen has been replaced. The molecule of benzene cannot, therefore, contain less than six atoms of that element. Moreover, since the quantities of hydrogen replaced by chlorine, or any other element or group of elements, always vary by one or more *sixths* of the whole and never by any smaller fraction, it is extremely improbable that the molecule contains more than six atoms of hydrogen. Hence the formula C_6H_6 must be assigned to benzene.

PHYSICAL METHODS

The so-called "physical methods" of determining molecular weights are all based on what are called by Ostwald the *colligative properties of matter*. Under certain conditions equal numbers of molecules produce equal effects, regardless of the chemical constitution and character of the molecules. Thus the volumes of gases under equal conditions of temperature and pressure are proportional to the number of gaseous molecules, and wholly independent of the composition of the molecules. The pressures exerted by equal volumes of gases at the same temperature are likewise proportional to the number of molecules which they contain. The occupation, under the same conditions of temperature and pressure, of equal spaces by equal numbers of gaseous molecules, without regard to their weight or chemical character, is a "colligative" property of gases. If equal volumes of different gases, when measured under like conditions, contain the same number of molecules, the weights of such equal volumes are related to each other as

are the molecular weights of the gases, and the determination of the density of a gas is equivalent to a determination of its molecular weight.

Other colligative properties of matter on which may be founded methods of determining molecular weights are observed in certain effects which are produced by substances in solution. The effects known as *osmotic pressure*, the lowering of the vapor tension of the solvent, and the depression of its freezing point are all proportional not to the weight of the different substances dissolved but to the number of the molecules contained in a unit volume of their solution. Under the same conditions equal numbers of molecules in a unit volume of a solution produce equal osmotic pressure, an equal lowering of the vapor tension of the solvent, and an equal depression of its freezing point. Hence we may determine the relative molecular weights of different substances by finding what quantities of them will produce these effects to the same degree; since these quantities are related to each other as are the molecular weights of the substances themselves.

I. Dumas' Method

At the present time the method of Dumas is rarely resorted to by chemists; it will therefore not be described in great detail.

By this method, which is applicable to easily volatilized liquids and solids, the molecular weight of a substance is deduced from the weight of a known volume of its vapor. The principle on which it is based is precisely the same as that which is employed in determining the densities and the molecular weights of gases by weighing. It is, in fact, a method for the determination of the densities of the vapors of substances at temperatures somewhat above their boiling points.

A glass balloon, Fig. 30, having a capacity of from 100 cc. to 250 cc., is carefully cleansed, and dried internally by attaching to it a calcium chloride tube through which air is alternately

pumped out and readmitted. The balloon is weighed, with a closed vessel of the same form and size as counterpoise, and the temperature of the air within the balance case and the height of the barometer are noted. The balloon is then warmed and its outlet is immersed in the liquid whose density is to be determined. On cooling, the liquid ascends into the balloon. After the introduction of several grams of the material, the balloon is placed in a bath which can be heated to a temperature considerably higher than the boiling point of the substance. Only the outlet is allowed to project above the liquid in the bath. The bath is heated to the required temperature and constantly stirred. When nearly all of the liquid has distilled out of the balloon, the temperature of the bath is kept as constant as possible until no more vapor issues from the apparatus. The outlet is then closed with a blowpipe, and a record is made of the temperature of the bath and of the height of the barometer. The balloon is removed from the bath, cleansed, and weighed, and the temperature within the balance case at the time of weighing and the height of the barometer are again recorded. To determine the capacity of the balloon, a file mark is made on the small tube near the end; the end of the tube is then immersed in mercury or recently boiled water, and the tip broken off. The liquid rises in the balloon, and should fill it completely, excepting, of course, the space occupied by the liquefied or solidified substance under investigation. As a rule, however, a bubble of gas remains in the top of the bulb, showing that the air was not all expelled by the vapors of the substance. The space occupied by the substance is so small that it may safely be neglected, but the volume of the residual air must usually be determined. The procedure by which the capacity of the apparatus and the volume of the air bubble are both ascertained is as follows: The balloon is submerged in the liquid until the air within is under atmospheric pressure, i.e. until the liquid within and that without are



FIG. 30

on the same level. The outlet is then closed with the finger and the bulb removed from the bath. The bulb is inverted and the air allowed to escape. If mercury has been used, the quantity of that metal required to complete the filling of the vessel is determined either by weighing or by measuring. The volume of the mercury thus introduced is equal to that of the air bubble. Finally, the capacity of the vessel is found by measuring or weighing the mercury which now completely fills it. If, on the other hand, water has been used, the vessel, after the escape of the air, is dried externally and weighed. It is then completely filled and again weighed. The difference between the two weights is the weight of the water whose volume is equal to that of the air bubble. The capacity of the vessel is calculated from the weight of the water which fills it. Having found the capacity of the balloon at the temperature of the last experiment, its capacity at the temperature of the bath when it was closed with the blowpipe is calculated in the usual manner. But there must be deducted from this the volume, at the same temperature, of the air which was not expelled by the vapors of the substance. The difference is the volume of the vapor at the temperature of the bath. As both the temperature of the bath and the height of the barometer were recorded at the time of closing the balloon, the theoretical volume of the vapor under standard conditions can be calculated.

The weight of the vapor is found by deducting from that of the closed apparatus both the weight of the bulb and that of the air which remained in it at the time of closing.

Having found the weight of the vapor and its theoretical volume under standard conditions of temperature and pressure, the former is divided by the weight of an equal volume of hydrogen under the same conditions. The quotient is the density of the vapor as compared with that of hydrogen. To find the molecular weight of the substance, its vapor density must be doubled.

The weight of the balloon enters twice into the calculation—first in finding its capacity, and secondly in finding the weight

of the vapor. But when the balloon was weighed in the first instance it was filled with air. To find its true weight, therefore, we must deduct that of the air which was weighed with it.

For the determination of the molecular weights of substances whose boiling points are too high to permit the use of glass, porcelain balloons have been employed. To close these, the flame of the oxy-hydrogen blowpipe is required.

The materials used in the bath must be such as to permit the raising of the temperatures of the vapors several degrees above the boiling points of the substances, since at temperatures near their boiling points the vapors of substances do not sufficiently obey the laws of Boyle and of Gay-Lussac.

II. The Method of Gay-Lussac

(Hofmann's Modification)

The method of Gay-Lussac is the converse of Dumas', since by it the molecular weight is deduced not from the weight of a known volume of the vapor but from the volume of the vapor of a known weight of the substance.

The procedure of the author of the method was as follows: A gas-measuring tube about 400 mm. in length was filled with mercury and inverted in an iron bath half full of the same metal. A thin glass bulb completely filled with a known weight of the substance was introduced by placing it under the open end of the tube. A glass cylinder, open at both ends, also wider and somewhat longer than the measuring tube, was placed in the bath and the space between the eudiometer and the cylinder was filled with water, oil, paraffin, glycerin, or some other liquid which could be heated to a sufficiently high temperature. The bath was then heated to the desired temperature and kept as nearly constant as possible until the volume of the vapor no longer increased. Finally there were recorded (1) the volume of the vapor, (2) the length of the mercury column within the measuring tube, (3) the temperature of the bath,

and (4) the height and temperature of the barometer. From these data the theoretical volume of the vapor under standard conditions could be calculated; and the weight of the substance divided by the weight of an equal volume of hydrogen gave the theoretical density of the vapor under the same conditions.

The method in its original form is no longer in use. The principal objections to it are (1) the mercury bath, the vapors of which are poisonous; (2) the difficulty of obtaining liquids to place between the measuring tube and the cylinder, which will remain transparent at high temperatures; and (3) the shortness of the measuring tube. The method could be used only for the determination of the molecular weights of substances having comparatively low boiling points. Most of these difficulties were overcome by a modification of the method which was proposed by Hofmann.



FIG. 31

Hofmann's Method

In the apparatus of Hofmann, Fig. 31, the measuring tube has a length of one meter. The advantage of the greater length is in the effect of diminished pressure on the boiling points of the substances whose molecular weights are sought. By enlarging the closed end of the tube and thus increasing the vacant space into which the substance evaporates, or by using very small quantities of material, it is practicable to determine the molecular weights of substances at temperatures several degrees below their boiling points under ordinary atmospheric pressure.

A glass jacket 40 mm. wide and 90 cm. long is placed over the measuring tube in the position shown in the figure, and connected at the top with a vessel containing a liquid of suitable boiling point. The vapor of the boiling liquid enters the jacket and passes out through the small tube at its lower end, heating the tube to the boiling point of the liquid. The substance is inclosed in a minute flask (with a ground-glass stopper),

which is just large enough to contain the quantity of material required for the determination.

The experiment is made in the following manner: The measuring tube is filled with mercury, inverted, and its open end immersed in a dish of the same metal. The height and temperature of the barometer and of the mercury column in the tube are recorded. The little flask containing the weighed quantity of the substance, which must completely fill it, is brought under the open end of the tube and allowed to ascend into the vacuum above. As it reaches the top of the mercury column, the stopper usually flies out of the flask. It is, however, immaterial whether it does so or not, since, unless the flask has been too tightly closed, it is soon expelled by the expanding material. The jacket is connected at the top with a flask or other vessel containing the liquid whose vapor is to heat the substance, and the exit tube at the bottom is attached to a condenser if necessary. The liquid employed depends on the temperature required. The liquids most frequently used are water, aniline (183°), naphthalene (217°), ethyl-benzoate (213°), and amyl-benzoate (261°). The liquid in the vessel connected with the jacket is boiled until the volume of the vapor in the measuring tube no longer increases. There are then recorded (1) the volume of the vapor, (2) the length of the mercury column above the lower end of the jacket, (3) the length of the mercury column below the jacket, i.e. that portion of the column which is not heated by the vapor of the boiling liquid, (4) the temperature, as nearly as it can be determined, of the mercury in the tube at a point halfway between the lower end of the jacket and the surface of the metal in the dish, and (5) the height and temperature of the barometer.

In finding the pressure under which the vapor was measured (by subtracting the corrected height of the mercury column in the measuring tube from the corrected height of the barometer) the two portions of the mercury column, having different temperatures, must be separately reduced to their length at

0°. It will be seen that the correction of the height of the mercury column is at best only approximate, owing to the lack of uniformity in the temperature of its different parts. Several plans for overcoming this difficulty have been proposed. Of these, the most obviously practicable one is to make the mercury cistern narrower and so to lengthen the jacket that it will inclose both the eudiometer and the cistern. The correction for the tension of the mercury vapor is made by subtracting from the corrected pressure the tension of the metal for the given temperature as found in the tables. The measuring tube should be calibrated, and if any considerable degree of accuracy is required, a correction for the expansion of glass must be applied.

The use of the Gay-Lussac method and of the Hofmann modification of it is necessarily limited to substances whose boiling points are considerably below that of mercury. At temperatures above 300° it cannot be employed with advantage owing to the great tension of the mercury vapor.

*Determination of the Volume of a Vapor by Means of the
Pressure which it Exerts*

The volume which a gas would have under standard conditions of temperature and pressure may be deduced from the pressure which it is found to exert when confined, at any given temperature, in a space of known volume. Hence the molecular weight of a volatile substance may be ascertained by determining the pressure exerted by a known weight of its vapor in a vessel of known capacity. Modifications of the Gay-Lussac method, which are based upon this principle, have been proposed by Bell and Teed (*Journal of the Chemical Society*, 1880, 1, 576), and by Malfatti and Schoop (*Zeitschrift für physikalische Chemie*, 1887, 159).

*Determination of the Volume of a Vapor by measuring the
Liquid or the Gas which it Displaces*

Methods of this kind are identical in principle with that of Gay-Lussac, since they differ from it only in the manner of determining the volume of the known weight of vapor. This is ascertained indirectly by measuring the volume of a liquid (usually mercury) or of a gas (air, hydrogen, or nitrogen) which the vapor displaces. The best known and most useful of these methods is that of Victor Meyer.

EXERCISE XIII

DETERMINATION OF THE MOLECULAR WEIGHT OF CHLOROFORM BY THE METHOD OF MEYER

The simplest form of the Meyer apparatus is shown in Fig. 32. It consists of three parts: (1) a glass tube in which a weighed quantity of the substance is converted into a vapor; (2) a glass, or better, in many cases, a metallic, mantle or bath, in the bottom of which is placed the liquid to be heated for the purpose of producing the required temperature; and (3) a graduated tube in which is collected the air or other gas displaced by the vapor of the substance. The total length of part 1 is about 800 mm. Its lower and larger end *b* has a capacity of about 100 cc. The narrower portion, between *b* and the cuplike enlargement at the top, has an internal diameter of about 6 mm. The side tube *a*, through which the displaced gas passes into the measuring tube, is joined to the main tube at a point about 100 mm. from the upper end of the latter. Its internal diameter should not much exceed 1 mm. The mantle has a diameter of 40 mm. and a length of 520 mm., exclusive of the bulblike enlargement at the lower end, the capacity of which is about 80 cc.

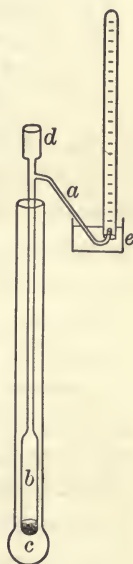


FIG. 32

Thoroughly cleanse the apparatus by washing it with alcohol, and then with ether which leaves no residue on evaporation. Attach a calcium chloride tube to *a*, insert a stopper through which is passed a long glass tube reaching to the bottom of *b*, and aspirate air through the apparatus until it is dry. Place a quantity of ignited asbestos in the bottom of *b*. Fill the bulb *c* nearly full of distilled water, and clamp the mantle in an iron stand at such a height that when the stand is upon the floor, the tube *a* will be a little above the top of the work table. Arrange all parts of the apparatus as indicated in the figure. Select a tightly fitting, singly perforated rubber stopper for *d*. Pass through it, from the upper end, a short glass tube provided with a ground stopcock. The tube need not have an external diameter of more than 5 mm. The channel through the stopcock



FIG. 33

should, however, be relatively large. Blow a bulb with a capacity of 0.3 or 0.4 cc. on the end of a thin small glass tube, Fig. 33. Weigh the bulb, immerse the open end of the stem in pure chloroform, and, by alternately warming and cooling the bulb, introduce from 0.2 to 0.3 cc. Dry the wet end of the stem with filter paper and close it in the flame. Weigh again. Pass the stem of the bulb through the stopcock, as shown in Fig. 33, and fix it in position by turning the latter until it presses lightly against the stem. Insert a stopper in *d*. Boil the water in *c* vigorously. Immerse the outlet of *a* in the dish of water *e*. When no more air issues from the apparatus, fill the gas-measuring tube with water and invert it over the outlet of *a*. Replace the stopper in *d* by the arrangement represented in Fig. 33, and, after about one minute, close the stopcock. The stem will be cut and the bulb containing the chloroform will fall upon the asbestos in the bottom of *b*.

The chloroform is converted into vapor, and a volume of air equal to that of the vapor is transferred from the upper part of the apparatus to the measuring tube. The air in passing through the water is cooled, and its volume when measured is therefore

smaller than that of the vapor of the chloroform. This, however, is not a source of error, since, if the air transferred and the chloroform vapor were of the same temperature, the latter would theoretically have suffered the same contraction in consequence of an equal lowering of temperature. The condition that the air forced out of the apparatus shall have the same temperature as the vapor whose density is to be determined is an essential one, for if its temperature is lower, the contraction in passing through the water will be too small, and the volume of the air collected in the measuring tube will therefore be too large. It cannot, however, be fully realized, since the air in the outlet tube, which is the first to be forced into the eudiometer, has a temperature very near that of the outside atmosphere. It is for this reason that the bore of *a* is made as small as is practicable.

The heating is to be continued until, for a space of two minutes, no more air is expelled. The air is then measured and its volume under standard conditions is found in the usual way. The weight of the chloroform divided by the weight of an equal volume of hydrogen is the theoretical density of the chloroform, and its density is one-half its molecular weight.

The original apparatus of Meyer was closed with a simple rubber stopper, which was removed at the time of introducing the substance and then quickly replaced. The compression produced by the insertion of the stopper caused the expulsion of a few bubbles of air which were allowed to escape before placing the eudiometer in position over the outlet. Under these conditions the success of the determination depended very much upon the good judgment and the alertness of the experimenter. Hence a number of modifications of the apparatus were soon proposed, which obviate the necessity of opening it at the time of dropping the substance into the heated chamber below. The accompanying Fig. 34, *A*, *B*, and *C*, represents some of the

modifications which are now in common use. In *A*, the tube containing the substance is released by turning the bent wire which passes through the stopper; in *B*, by turning the stopcock; and in *C*, by drawing to the left the wire in the horizontal tube. A distinct disadvantage in all of these devices is the necessity of introducing the substances in open tubes, and of leaving them for some time exposed to a more or less elevated temperature. If tubes with ground-glass stoppers are substituted for the open ones, the determinations are often lost in consequence of their failure to release the stoppers even when heated above the boiling points of the substances.

These difficulties are obviated in the case of liquids by using the arrangement prescribed in the preceding exercise. If the

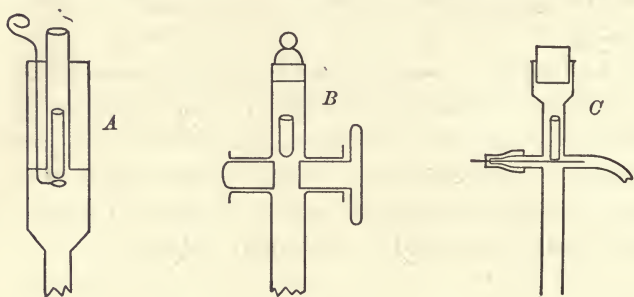


FIG. 34

substance is a solid, a narrow tube is closed at one end and then drawn out at a point near the closed end, leaving a passage just large enough for the introduction of the material. The tube is weighed, the substance introduced, and its weight ascertained. The tube is then fused off at the proper distance from the substance, leaving a stem which is passed through the stopcock in the manner already described.

When a substance is liable to be attacked by oxygen at the temperature required for the determination of its molecular weight, the air in the apparatus is displaced by some other gas, such as nitrogen or hydrogen. And when the temperatures are

too high to permit the use of glass vessels, an apparatus of platinum or of porcelain is employed. The following list contains the names and boiling points of some of the substances which are used in the bath of the Victor Meyer apparatus. Water (100°), amyl-alcohol (130°), xylene (137° to 143°), aniline (182.5°), ethyl-benzoate (213°), amyl-benzoate (261°), diphenyl amine (310°), mercury (357.25°), sulphur (448.4°), phosphorus pentasulphide (518°), stannous chloride (606°). For the determination of molecular weights at still higher temperatures, a gas or a coal furnace is employed.

THE FREEZING-POINT METHOD

When a substance is dissolved in a liquid the freezing point of the latter is lowered, and the observed depression is, in general, very nearly proportional to the concentration of the solution. In other words, if one gram of sugar is dissolved in 100 grams of water, the latter will no longer freeze at 0° , the freezing point of pure water, but at some lower temperature; if two grams of sugar are dissolved in the same quantity of water, the observed depression of the freezing point will be double that of the solution containing one gram, etc.

The depression of the freezing point which is observed in a one-per-cent solution of a substance in any given liquid, i.e. when one gram of the substance is dissolved in 100 grams of the liquid, is called the *specific depression* of the freezing point of the liquid for the particular substance.

If different substances, in quantities proportional to their respective molecular weights, are dissolved in equal weights of any given liquid, the different solutions will as a rule be found to have the same freezing point. From this fact is drawn the conclusion that the extent of the depression in the case of any given liquid is determined solely by the numerical ratio of the molecules of the dissolved substance and of the solvent. In other words, equal numbers of molecules, when dissolved in

equal quantities of any given liquid, produce an equal lowering of the freezing point whether the molecules are of the same kind or of different kinds.

The depression of the freezing point which results from dissolving in 100 grams of a liquid a number of grams equal to its molecular weight is called the *molecular depression* of the freezing point of the liquid for that substance. The molecular depression is equal to the product of the specific depression and the molecular weight of the substance. For any given liquid the molecular depressions for different substances have a nearly constant value. This constant may be determined experimentally by dissolving in a known weight of a liquid a weighed quantity of some substance of known molecular weight, and ascertaining the depression of the freezing point; or it may be calculated, when the requisite data are at hand, by the equation of Van't Hoff:

$$C = 0.02 \frac{T^2}{W}, \text{ in which}$$

C is the constant to be found,

T the absolute freezing point of the liquid, and

W its latent heat of fusion.

The following table gives the molecular depression of the freezing point of several liquids as found by experiment and by calculation.

	BY EXPERIMENT	BY CALCULATION
Water	18.8	18.7
Acetic acid	39.0	38.8
Formic acid	28.0	28.4
Benzene	50.0	53.0
Nitrobenzene	70.0	69.5
Phenol	74.0	77.0
Naphthalene	69.0	69.4

If the molecular depression of the freezing point of any solvent is divided by the molecular weight of the same, the quotient is the depression which one molecule of any substance, behaving normally in solution, will produce in 100 molecules of

the solvent. This value is, of course, constant for any given solvent, but, contrary to the conviction of Raoult, it varies with different solvents.

There are many exceptions to the rule that equi-molecular quantities of different substances produce, in a fixed quantity of any given solvent, an equal lowering of the freezing point. For example, when water is used as a solvent, molecular-equivalent quantities of the class of bodies known as electrolytes — acids, bases, and salts — produce a much greater depression of the freezing point than equivalent quantities of indifferent substances, such as the sugars and urea. Hydrochloric, hydrobromic, hydriodic, and nitric acids, also the hydroxides and the halogen salts of the metals of the alkalies, produce in dilute aqueous solutions nearly twice the normal depression of the freezing point. This conduct on the part of electrolytes is not regarded as invalidating the law that equal numbers of molecules produce equal effects. It is supposed, rather, to indicate that, in aqueous solutions, the molecules of the bodies in question suffer a certain kind of dissociation. In benzene, nitrobenzene, and ethylene bromide, on the other hand, the alcohols and the organic acids produce only about one-half the normal depression of the freezing point. This conduct is supposed to be due to the existence in such solutions of double molecules, e.g. $(C_2H_4O_2)_2$, instead of $C_2H_4O_2$, since the same substances in other solvents produce normal depressions.

To determine the molecular weight of any substance by the freezing-point method, a small weighed quantity of it (g) is dissolved in a weighed quantity of some solvent (G) in which it is supposed to behave normally, and whose molecular depression (c) is known. The freezing point of the solvent is determined before (t) and after (t_1) the introduction of the substance. The depression ($t - t_1$) is represented by d . Having found the depression d , which g grams of the substance produce in G grams of

the solvent, it is necessary to find how much of it would produce an equal depression in 100 grams of the solvent, since the constant c is calculated for that weight of the liquid. This is done by means of the proportion

$$x : 100 :: g : G. \quad x = \frac{100g}{G}.$$

If $100 \frac{g}{G}$ grams of the substance produce the depression d in 100 grams of the solvent, the quantity (m) which will produce the molecular depression is $100c \frac{g}{Gd}$, since

$$m : 100 \frac{g}{G} :: c : d. \quad m = 100c \frac{g}{Gd}.$$

The process by which c is obtained is such that m is equal to the molecular weight of the substance. The formula $m = 100c \frac{g}{Gd}$ is general, and to obtain the molecular weight of any substance it is necessary only to substitute in it the proper numerical values of C , g , G , and d .

The method is applicable only to quite dilute solutions, and appears, in general, to give the most satisfactory results in those which are about one-tenth normal.

The thermometer which is used both in the freezing-point and in the boiling-point methods of determining molecular weights was devised by Beckmann, Fig. 35. Its characteristic feature is the reservoir at the top to which a portion of the mercury in the bulb may be transferred. The scale is divided into hundredths and has a total range of only five or six degrees. It is practicable, by transferring portions of mercury from the bulb below to the reservoir above, or from the reservoir to the bulb, to adjust the instrument for use at widely different temperatures. Suppose, for instance, that it is required to measure changes of temperature between 34° and 38° , and that the range of the scale is nominally 6° . The bulb is placed in water having a temperature of about 40° . If the mercury

rises to the top of the scale or slightly above it, there is no need of readjustment, since, in that case, the upper end of the mercury column will be within the scale both at 34° and 38° . If the mercury rises and flows over into the reservoir, the column, when the mercury ceases to expand, is broken off at its highest point by striking the bulb against the palm of the hand. The thermometer will then register any temperature between the desired limits. If, on the other hand, the mercury on being heated to 40° does not enter the scale, or ascends only part way through it, a portion of the metal in the reservoir must be transferred to the bulb. This transference is accomplished in the following manner: The mercury above is forced into the upper end of the reservoir by striking the top of the thermometer against the hand. The bulb is then heated until the mercury in it rises and joins that in the reservoir. Finally, the bulb is placed in water of 40° , and the column broken in the manner previously described.

It is to be observed that the divisions upon the scale of the Beckmann thermometer have a somewhat variable value owing to the fact that the quantity of mercury in the bulb varies according to the temperatures for which the thermometer is adjusted. In other words, the value of the scale as a measure of changes of temperature (of depressions and elevations) depends on the quantity of the contracting or expanding mercury in the bulb. If the quantity is diminished, as it must be for the higher temperatures, the value of the scale is correspondingly increased; if, on the other hand, a portion of the mercury is transferred from the reservoir to the bulb to prepare the instrument for use at lower temperatures, the value of the scale

FIG. 35

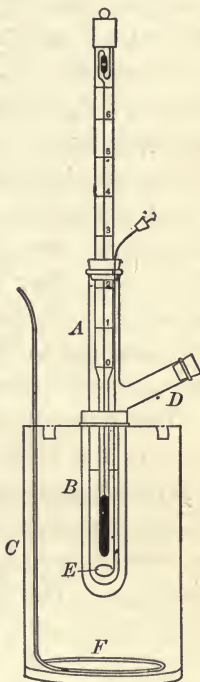


FIG. 36

is diminished. Errors from this source may require attention when a thermometer is used for widely separated temperatures; as, for example, when the same instrument is employed for the determination both of freezing and of boiling points.

The method which is here suggested for the correction of such errors is as follows: The value of the scale, when the mercury in the bulb is in the vicinity of 0° , is determined by comparing the instrument with a standard thermometer. If now the thermometer is used at a higher temperature, requiring a transfer to the reservoir of a portion of the mercury in the bulb at 0° , the observed depressions or elevations, in terms of the value which the scale has at 0° , are to be multiplied by $1 + t^{\circ}\gamma$, in which

t° is the higher temperature, and

γ the apparent expansion of mercury in glass, i.e. the difference between the cubical expansion of mercury and of glass. If, on the other hand, the instrument is used at a lower temperature, $-t^{\circ}$, requiring a transfer of some of the mercury in the reservoir to the bulb, the observed depressions or elevations are to be multiplied by $1 - t^{\circ}\gamma$.

The determination of the value of the scale, when the mercury in the bulb is in the neighborhood of 0° , is made in the following manner: The mercury above is forced into the end of the reservoir nearest the bulb, and the mercury in the bulb is warmed until it rises and forms a junction with that in the reservoir. The bulb is placed in water having a temperature of 7° or 8° , and, when the mercury comes to a standstill, the thread is broken off at its highest point. The bulb is now placed in ice water. The top of the thread should recede nearly to the zero mark of the scale. If it does not, or if it descends below that point, the experiment is repeated, using warmer or colder water for the first immersion, as the case may require.

The following considerations will serve to explain the proposed method of correcting the Beckmann thermometer. Suppose an instrument of this kind is so adjusted that the end of the thread is within the scale when its bulb is in ice water.

Depressions and elevations of temperature in the vicinity of 0° can now be measured in terms of the scale. Suppose, however, it is desired to measure changes of temperature around some higher temperature t° . A portion of the mercury in the bulb must be transferred to the reservoir, and the value of each scale division is thereby increased in the same proportion as the quantity of the mercury in the bulb is diminished. If we let m represent the quantity of mercury in the bulb when the instrument is adjusted for 0° , then the quantity in the bulb when it is adjusted for the higher temperature t° will be $m - mt^\circ\gamma$. The values of a scale division are, of course, inversely proportional to the quantities of mercury forced into the stem from the bulb in consequence of a given rise of temperature, and these are directly proportional to the quantities in the bulb. If we represent by unity the quantity of mercury which will enter the stem in consequence of a given rise of temperature when the instrument is adjusted for 0° , then the quantity x , which will enter when it is adjusted for t° , will be found by the proportion

$$m : m - mt^\circ\gamma :: 1 : x.$$

$$x = 1 - t^\circ\gamma.$$

That is, if we know the value of the scale when the temperature is in the vicinity of 0° , we can find its value in the vicinity of any higher temperature t° by multiplying by $1 + t^\circ\gamma$.

In the same way it may be shown that, knowing its value in the vicinity of 0° , we can find its value at any lower temperature $-t^\circ$ by multiplying by $1 - t^\circ\gamma$.

The mercury exhibits a strong inclination to stick in the capillary tube of the Beckmann thermometer. This tendency manifests itself more strikingly with a falling than with a rising temperature. It should be overcome, as far as possible, whenever a reading is to be made, by tapping the thermometer near the top with some hard object. A device for this purpose, which has been used with advantage, is a minute vibrating electrical hammer attached to the top of the instrument.

Figures 36 and 37 represent the forms of the Beckmann apparatus which are in common use for the determination of

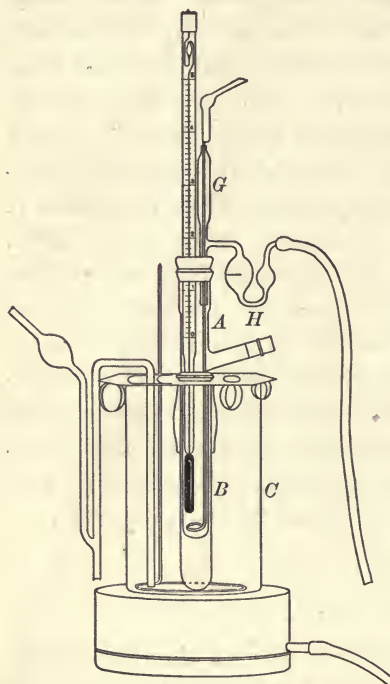


FIG. 37

molecular weights by the freezing-point method. The tube *A*, Fig. 36, which contains the solvent whose freezing point is to be determined both before and after the introduction of the substance, is separated from the freezing mixture in *C* by the wider tube *B*. The substance to be investigated is introduced through the side tube *D*. The stirrers *E* and *F*, the former of which is best made of stout platinum wire, are employed to equalize the temperature of the liquid in *A* and of the freezing mixture in *C*. The apparatus represented in Fig. 37 is used when the solvent, like glacial acetic acid, is hygroscopic. The only essential difference between it and

that in Fig. 36 is the arrangement *G*, through which dry air is passed during an experiment. The tube *G* is of such internal diameter that the stirrer which passes through it can be worked up and down without friction. To its side is attached the bulb tube *H*, in which a small quantity of concentrated sulphuric acid is placed. The acid is prevented from spattering into the solvent by a disk which is fastened in a horizontal position to the wall of the larger bulb. The air is dried before entering *H* by passing it over pumice stone which has been moistened with sulphuric acid.

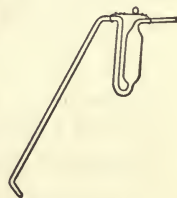


FIG. 38

Solid substances which dissolve readily are best introduced in the form of compressed tablets. These are easily prepared by stamping the requisite quantity of the loose material in a small pastil press such as is used in making medicinal tablets.

Liquids are introduced by means of the pipette shown in Fig. 38.

EXERCISE XIV

DETERMINATION OF MOLECULAR WEIGHTS BY THE FREEZING-POINT METHOD

1. UREA

Bring into the tube *A* a weighed quantity of distilled water which will somewhat more than suffice to cover the bulb of the thermometer, and into *C* a mixture of broken ice, coarse salt, and water. Remove *A* from *B* and immerse it for a time in the freezing mixture. Return it, after drying the outside, to its place in *B*. Let the water in it cool somewhat below the freezing point, and then stir vigorously until ice begins to form, taking care not to let the stirrer rub against the bulb of the thermometer. The thermometer will rise a little and then become stationary. The highest temperature is the true freezing point of the water. Remove the tube *A* after considerable ice has formed, and continue to stir until the mercury in the thermometer is observed to rise. Repeat the experiment several times. Remove *A* and introduce through the side tube in compact form a quantity of pure urea which is calculated to give a nearly one-twentieth molecular-normal solution. Stir until the urea is dissolved and the ice has nearly, but not quite, all melted. Return *A* to its place in *B*. Let the solution cool for a short time and then stir until ice again forms. The thermometer will rise, become stationary for a few moments, and then begin to fall. The highest temperature reached is the one to be recorded. Remove *A*, stir vigorously, and observe the thermometer while the ice is melting. Repeat the experiment several times.

Add three other small quantities of urea, each about equal to the first, and determine the freezing point after each addition.

Calculate the molecular weight of urea from the depression of the freezing point, which was observed for each concentration, using 18.9 as the molecular depression of water. Deduce also from the observed depressions and the known molecular weight of urea the molecular depression of the freezing point of water.

If stirring the under-cooled solution fails to induce freezing, the difficulty may be overcome by introducing a minute fragment of ice. The effect of so doing upon the concentration of the solution is, of course, insignificant. The same course is to be followed when other solvents than water are used. If no crystals of the solvent are at hand, they may be prepared by freezing a little of the pure liquid in a small test tube. A convenient method for the preparation of crystals to be used in starting the freezing of the solvent has been described by Beckmann (*Zeitschrift für physikalische Chemie*, 7, 329).

The concentration of the solution is, of course, increased by the freezing of a portion of the solvent. This explains the falling of the thermometer which is observed to follow its rise when freezing begins. Since the quantity of ice which will be formed is determined by the amount of the under-cooling, the error due to such an increase in concentration may be diminished by cooling the solution only slightly below its freezing point. The increase in concentration may be calculated by the formula

$$r = \frac{c\theta}{\lambda}, \text{ in which}$$

r is the fraction of the solvent which solidifies in consequence of the under-cooling,

θ the degree of the under-cooling which preceded solidification,

c the specific heat of the solvent, and

λ the heat of solidification of a unit quantity of the solvent.

2. CANE SUGAR

Proceed as directed under 1, using water as the solvent and "rock candy" as the material to be experimented upon.

3. CHLOROFORM

The glacial acetic acid which is used as the solvent in this experiment must be carefully protected from the moisture of the air. It is advisable to use the apparatus represented in Fig. 37, and to conduct air dried by sulphuric acid through *G*. Glacial acetic acid, when pure, melts at 16.75° . It is, however, hygroscopic and is therefore usually found to fuse at a lower temperature. The presence in it of a small quantity of water does not interfere with its use as a solvent, provided the same is not acquired during the course of an experiment.

Glacial acetic acid gives normal results with nearly all substances which dissolve in it without chemical action. The molecular depression of its freezing point is 39.

THE BOILING-POINT METHOD

If a nonvolatile substance is dissolved in a volatile liquid, the vapor tension of the latter is diminished and its boiling point is therefore raised. The effects produced by substances in solution upon the vapor tension and boiling points of liquids are in all respects analogous to those produced upon their freezing points.

In the case of a given solvent and soluble substance, the lowering of the vapor tension at any given temperature and the consequent elevation of the boiling point are proportional to the concentration of the solution.

Again, equi-molecular quantities of different substances, when dissolved in the same weight of any given liquid, produce an equal lowering of the vapor tension, and consequently an equal elevation of the boiling point of the solvent.

No practicable method has yet been devised for the determination of molecular weights by measuring directly the effect of

substances in solution upon the vapor tension of the solvents. It has been found easier to utilize for this purpose the temperatures of equal-vapor tension, i.e. the boiling points of the solvents.

The definitions employed are similar to those which were given in connection with the freezing-point method.

1. *The specific elevation* of the boiling point of any liquid is that which is observed when 1 gram of a substance is dissolved in 100 grams of the solvent. Obviously the specific elevations produced by different substances are inversely proportional to the molecular weights of the substances.

2. *The molecular elevation* of the boiling point of a liquid is that which is produced when a number of grams of a substance equal to its molecular weight is dissolved in 100 grams of the solvent. In the case of any given substance, the molecular elevation is equal to the product of the specific elevation and the molecular weight of the substance. It is a constant for any given solvent in the same way and with the same limitations as the molecular depression of the freezing point. Like the latter, it may be determined experimentally by operating with weighed quantities of the liquid and of some substance of known molecular weight, or it may be calculated by means of the formula

$$C = 0.02 \frac{T^2}{W}, \text{ in which}$$

C is the constant to be found,

T the absolute boiling point of the liquid, and

W its latent heat of vaporization.

The following table gives the molecular elevation of the boiling points of several liquids.

Ether	21.1	Benzene	26.7
Acetone	16.7	Water	5.2
Chloroform	36.6	Acetic acid	25.3
Carbon bisulphide	23.7	Ethylene bromide	63.2
Alcohol	11.5	Phenol	30.4
Ethyl acetate	26.1	Aniline	32.2
Methyl alcohol	9.2	Isopropyl alcohol	12.9

If the molecular elevation of any solvent is divided by the molecular weight, the quotient is the elevation of the boiling point which one molecule of any substance, not dissociating in solution, will produce in 100 molecules of the solvent.

The method of deducing the molecular weight of a substance from the effect which it produces on the boiling point of a liquid is the same as that employed in the freezing-point process. If g grams of the substance produce an elevation e in G grams of the solvent, then the quantity of the substance which will produce the same elevation in 100 grams of the solvent is $100 \frac{g}{G}$; for $x : 100 :: g : G$. Again, if $100 \frac{g}{G}$ grams of the substance produce the elevation e in 100 grams of the solvent, the quantity which will produce the molecular elevation is

$$100 C \frac{g}{Ge}, \text{ since}$$

$$m : 100 \frac{g}{G} :: C : e. \quad m = 100 C \frac{g}{Ge}.$$

m represents the molecular weight of the substance, and its value is found by substituting in the formula the numerical values of C , g , G , and e .

As might be expected from their behavior when tested by the freezing-point method, the class of bodies known as electrolytes gives, when dissolved in water, abnormal elevations of the boiling point.

In benzene, chloroform, and carbon bisulphide, certain bodies, especially hydroxyl compounds, give less than the calculated elevation of the boiling point. This is supposed to be due to the existence in such solutions of complex molecules, consisting either of the dissolved substance and the solvent, or of the former only. The results, however, become more nearly normal with increasing dilution. When a substance of unknown molecular weight is to be investigated, it is safer to test its effect upon the boiling points of several liquids.

With reference to the selection of a solvent for any particular determination, it is to be observed that the liquid chosen should be one in which the substance is very readily soluble, also that its boiling point should be, in general, not less than 130° or 140° lower than that of the substance to be investigated. If the boiling points of the substance and of the available solvents are too near together, the freezing-point rather than the boiling-point method should be employed.

As a rule, the best results are obtained when ether, alcohol, ethyl acetate, acetone, acetic acid, formic acid, thymol, and phenol are used as solvents.

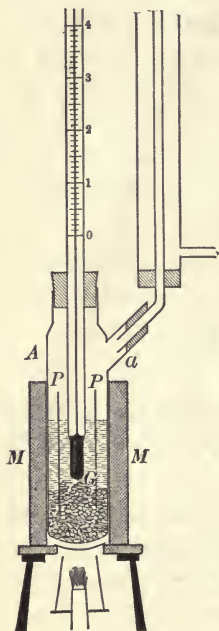


FIG. 39

A number of forms of apparatus for the determination of molecular weights by the boiling-point method have been devised and recommended. Only one of them, that of H. C. Jones, Fig. 39, will be described here. It consists of a glass tube *A*, 180 mm. in length and 40 mm. in diameter, to the side of which is attached the smaller tube *a*. It is contracted at the top to a diameter of about 27 mm. and ground to receive a light glass stopper, which is inserted when the apparatus is to be weighed. The tube is filled with glass beads to a height of 30 or 40 mm., and into these is pressed to a depth of 15 or 20 mm. the platinum cylinder *P*, which has a length of 80 mm. and a diameter of 25 mm. The

space within the platinum cylinder, under and around the bulb of the thermometer, is filled with scraps of platinum foil whose corners have been bent in different directions to prevent too close packing and whose edges have been serrated to facilitate the escape of vapor. The condenser tube which enters at *a* is provided at the top with a U-tube containing some drying agent. The apparatus is surrounded by a jacket of asbestos *M*, 120 mm.

in height and 15 mm. in thickness, which rests on an asbestos board having a hole in the center. The hole is covered with a piece of wire gauze.

EXERCISE XV

DETERMINATION OF MOLECULAR WEIGHTS BY THE BOILING-POINT METHOD

1. IODINE

Adjust the thermometer so that the upper end of the mercury column will be in the lower part of the scale at the boiling point of ether. Carefully cleanse and dry the apparatus, especially those parts which will afterwards come in contact with the solvent, and arrange the beads, platinum cylinder, and platinum scraps as indicated in the description of the apparatus. Close *A* with the ground-glass stopper and the side tube *a* with an ether-tight cork and weigh. Introduce somewhat more anhydrous ether than is necessary to cover the bulb of the thermometer when in place and weigh again. If a balance of sufficient capacity to permit the weighing of so heavy a load is not available, the solvent must be weighed separately. Arrange everything as shown in the figure; heat cautiously and determine the boiling point of the ether. Several observations should be taken at considerable intervals of time, and the height of the barometer should be recorded with each observation of the temperature. The thermometer must be vigorously jarred just before reading, and the reading should be made after a rise rather than after a fall of temperature. This may always be done by allowing the liquid to cool a little and then reheating it to its boiling point.

Introduce through the side tube, when the ether is cold, from 0.5 to 0.7 gram of dry resublimed iodine, and again determine the boiling point, recording, as before, the height of the barometer. Afterwards introduce several other small weighed

portions of iodine, from 0.1 to 0.2 gram, determining the boiling point after each addition. Finally, when the apparatus has cooled, weigh again in order to ascertain whether any ether has been lost during the experiment.

Calculate the molecular weight of iodine from the results of the individual determinations and from the total observed elevation of the boiling point, using 21.1 as the molecular elevation of the boiling point of ether. Calculate also from the observed elevation and the known molecular weight of iodine the molecular elevation of the boiling point of the solvent.

2. NAPHTHALENE

Proceed exactly as directed under 1.

The boiling solution has something more than its calculated concentration, owing to the absence of a portion of the solvent in the form of vapor and of returning liquid. Errors from this cause are reduced to a minimum by carefully regulating the rate of boiling, which should not be more rapid than is necessary for the maintenance of a constant temperature and to prevent the overheating of the liquid.

The temperature indicated by the thermometer varies somewhat according to the depth to which the bulb is submerged in the boiling liquid. It is therefore well to maintain the same degree of submergence through the whole course of any single determination of a molecular weight.

The most serious difficulty which is encountered in the use of the boiling-point method is the variability of atmospheric pressure. A rise or fall of one millimeter in the barometer is followed by a change of boiling point amounting in the case of most liquids to nearly $.03^{\circ}$. It is obvious that the real results of a determination may be wholly masked in consequence of such barometric fluctuations as frequently occur within the time required for an experiment. This difficulty may be met more or less successfully in various ways.

1. A second apparatus containing the solvent only may be placed beside that in which the determination is made. If the liquids in both are boiled under the same conditions, as nearly as possible, and if the two thermometers are read simultaneously, the observed fluctuations of the boiling point of the pure solvent may be applied as corrections to the observed elevations of the boiling points of the solution.

2. A pressure regulator may be employed (see *Zeitschrift für physikalische Chemie*, 11, 25).

3. All observed boiling points may be corrected to standard pressure by means of the formula

$$\text{Correction} = \pm n \frac{Tc}{50}, \text{ in which}$$

T is the absolute boiling point of the liquid under standard pressure,

c a constant depending upon the chemical nature of the solvent, and

n the difference in millimeters between 760 and the observed height of the barometer.

The value of c for several different liquids, also the meaning of the formula and the manner of using it, will be found on page 191 of the second edition of Landolt and Boernstein's *Physikalisch-Chemische Tabellen*.

CHAPTER VIII

THE PURIFICATION OF SUBSTANCES

The preparation of substances in pure condition and the maintenance of their purity are obviously matters of the highest importance in quantitative chemistry; nevertheless, but little of a comprehensive character which is likely to be useful to the student can be said upon these subjects. The processes of purification and the measures adopted to prevent contamination must be constantly modified to suit the conditions, i.e. the character of the substances to be purified and the nature of the impurities to be removed or guarded against. Hence a minute knowledge of the reactions of the substances concerned, rather than of general rules, and vigilance are essential to a judicious selection of methods and a successful execution of them. There are, however, a few operations, such as evaporation, recrystallization, filtration, washing upon filters, etc., which are so frequently employed in the preparation of materials in pure condition that some observations regarding them may be of advantage.

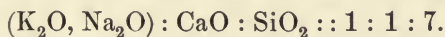
1. EVAPORATION OF LIQUIDS

When a solution is to be evaporated for the purpose of increasing its concentration or for the purpose of purifying a substance by recrystallization, attention should be paid to the possible action of the solvent and the dissolved matter upon the material of the containing vessel. In general, a porcelain vessel is less readily attacked by reagents than one of glass, and platinum resists their action still better than porcelain. Glass and porcelain are much more readily attacked by alkaline than by neutral or acid solutions, and less readily by those which

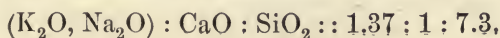
are moderately acid than by those which are neutral. Hence, as a rule, if such a course is practicable, an alkaline or even a neutral solution which is to be concentrated in glass or porcelain should be slightly acidified. This may often be done without disadvantage when the substance whose purity is an object of concern is a salt, since the presence in a solution of a slight excess of the same acid as that in the salt is frequently unobjectionable.

Most of the glass used in a chemical laboratory is essentially a silicate of the alkali metals, potassium and sodium, and of calcium. The character of the glass, especially as regards its power to resist the action of reagents, depends upon the ratio of these three constituents, and apparently more upon the ratio of the alkaline and alkaline-earth bases to each other than upon that of the silica to the sum of the bases. An increase in the proportion of the calcium improves the glass in respect to its ability to resist the action of reagents, but at the same time increases the difficulty of working it in the flame. An increase in the proportion of the alkalis produces precisely the opposite effects; that is, glass containing a relatively high percentage of the alkalis is easily worked, and is also readily attacked by reagents. The injurious effect of a large proportion of the alkalis may however be diminished to some extent by increasing the proportion of the silica. A soda glass is said to resist the action of reagents better than a potash glass of analogous composition.

Two varieties of glass of established excellence for chemical purposes have been put upon the market. One of these, the so-called Stas glass, is characterized by its great resisting power, and also, unfortunately, by the difficulty of working it in the flame. Its composition is represented by the ratio



The second variety, known as Weber's glass, has also a considerable resisting power and is worked with a fair degree of ease. Its composition is represented by the ratio



A third variety of glass known as "the Jena utensil and tube glass for chemical and physical uses" has within recent years entered into competition with the long-known and highly valued Bohemian or "hard" glass. According to one certificate of official examination, this glass was found to excel the best Bohemian in the following ratios:

4 to 5 : 1, when treated with water at 20°,
 11 to 12 : 1 " " " " " 80°,
 3 : 1 " " " 2-normal soda solution.

When treated for 6 hours with a normal solution of sulphuric acid at 100°, neither glass was sensibly attacked. On the other hand, as regards resistance to the action of a 2-normal solution of sodium hydroxide, the Bohemian was found to excel the Jena glass in the ratio of 3 : 2. The Jena glass is said to be greatly superior to the Bohemian in respect to its power to withstand sudden changes of temperature.

The question of the composition of the glass employed for chemical purposes, and the relation of its qualities, good and bad, to composition is worthy of much more general and systematic attention in the laboratory than has hitherto been given to it. The following references to published communications may be of use to those who wish to learn what observations upon this subject have already been made public.

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- F. Mylius, *Zeitsch. anal. Chem.*, **30**, 247.
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F. Mylius and F. Foerster, *Zeitsch. für Instrumentenkunde*, **9**, 117 (*Zeitsch. anal. Chem.*, **30**, 317).
Zeitsch. anal. Chem., **31**, 24.
F. Kohlrausch, *Ann. der Phys. und Chem. (N.F.)*, **44**, 577 (*Zeitsch. anal. Chem.*, **31**, 421).
Ber. d. d. chem. Ges., **24**, 3560; **26**, 2998 (*Zeitsch. anal. Chem.*, **34**, 591).
E. Pfeiffer, *Ann. der Phys. und Chem. (N.F.)*, **44**, 239.
F. Foerster, *Zeitsch. anal. Chem.*, **33**, 299, 322, 381.
A. Winkelmann and O. Schott, *Zeitsch. für Instrumentenkunde*, **14**, 6 (*Zeitsch. anal. Chem.*, **34**, 591).

The danger that exposed solutions will become contaminated by the dust in the air and by the volatile reagents which are used in the laboratory is too obvious to require more than a passing mention. There is, however, one source of contamination which is not so generally recognized as it deserves to be. It is the sulphur in the illuminating gas. Any aqueous solution or basic substance which is heated in an open vessel over a lamp burning illuminating gas is in danger of becoming contaminated with sulphuric acid unless precautions are taken to divert the products of combustion. For this reason it is often better to evaporate liquids and to heat strongly basic substances over an alcohol lamp rather than over a Bunsen burner.

The so-called *bumping* of evaporating solutions is frequently a source of trouble. The cause of the phenomenon is the superheated condition of the liquid in that part of the vessel to which the heat is applied, usually the bottom, which increases to a certain degree, when a large amount of vapor suddenly forms and escapes through the liquid above with explosive violence. In the case of actively boiling liquids it is frequently helpful to introduce scraps of platinum foil with serrated edges, or bits of broken glass, or anything in fact which, owing to its numerous sharp edges and points, facilitates the escape of vapor from a hot liquid. The disturbance usually ceases if the vessel is placed in a bath of any kind so that the

liquid is heated uniformly upon all sides. Hence the utility of flasks surrounded with a net of woven wire, and of metallic vessels for the evaporation of liquids which exhibit this propensity. If a liquid is to be rapidly evaporated in an open metallic vessel, e.g. a platinum crucible or dish, the vessel should be tilted to one side and the flame applied to it above the surface of the liquid instead of below it. Any arrangement is advantageous which enables one to apply the heat principally to the upper portions of an evaporating liquid, or at least as much to the upper as to the lower portions. A bath which is serviceable when a liquid of not too high boiling point is to be evaporated in a beaker or other vessel of similar form is quickly made in the following manner: A long strip of copper wire gauze, whose width is somewhat greater than the height of the vessel, is tightly wound several times around the beaker and fastened with wire. The lower edges are turned inward until they meet, and hammered into a flat and compact bottom. The bath is filled to a depth of 10 or 15 mm. with loose asbestos, and its vertical outside covered with several thicknesses of asbestos paper. It is best heated on an iron plate. A simple but often useful device for applying heat to a low-boiling liquid at any desired point is a copper wire which is wound around the containing vessel. The ends of the wire are allowed to extend to a safe distance from the apparatus and, singly or twisted together, are heated with a lamp or by other suitable means. The arrangement is more effective if the surface to be wound with the wire is first covered with copper foil.

2. RECRYSTALLIZATION

When a hot saturated solution of a substance is cooled for the purpose of purifying the substance by recrystallization, the liquid should be stirred while the crystals are forming. In this way small crystals are obtained which are less likely to inclose mother liquor than the large ones which form in tranquil solutions.

Crystals collected upon paper filters are liable when removed to become contaminated with shreds of the paper. It is therefore better, as a rule, to collect the product of a recrystallization in a funnel in the bottom of which only a platinum cone or a perforated porcelain disk has been placed. If the filtrate is found to contain too many crystals, it may be again passed through the filter.

It is important, after each recrystallization, to remove from the crystals as completely as possible the adhering mother liquor. To this end a filter pump should be employed, and the mass in the funnel should be made as compact as possible by pressing and stamping with a pestle or other hard object. Finally, when no more liquid can be extracted by means of the pump, the crystals should be immediately transferred to a clean unglazed porcelain plate and then stirred until they are thoroughly dry. If the substance is not too soluble, the crystals, after removal of the mother liquor by the pump, may be moistened with pure water, allowed to stand for a short time, and again freed from mother liquor by pumping. In some cases the adhering mother liquor may be removed by washing the crystals with a liquid, e.g. alcohol, in which they are insoluble, or only slightly soluble.

Many substances containing water of crystallization, such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{C}_2\text{O}_4\text{H}_2 \cdot 2\text{H}_2\text{O}$, etc., which appear to be stable in the air, really exert a vapor tension at ordinary temperatures, as is proved by their efflorescence when placed in desiccators. Such substances can only be air-dried, and that only at ordinary temperatures, or dried over desiccating materials which have a vapor tension equal to or greater than their own.

The handling, in quantitative operations, of substances having water of crystallization or capable of acquiring it from a moist atmosphere requires intelligent management. One general rule, however, may be given with respect to their treatment, namely, that substances which contain water of crystallization, but are not hygroscopic, must at all times be surrounded by an

atmosphere in which the tension of water vapor is sufficient to prevent their dissociation, while substances which are capable of absorbing water must be kept in an atmosphere in which the tension of water vapor is just equal to their own. It will be readily understood that it is not often practicable to conform to the latter condition if the hygroscopic substances contain any water whatsoever; hence such materials, as a rule, must be completely freed from water and preserved thereafter in a dry atmosphere. This course, however, often leads to difficulties, especially in the case of salts, many of which, when heated to the temperatures requisite for their complete dehydration, decompose with loss of acid and formation of more or less of basic salts.*

3. DESICCATION

In drying substances to a constant weight we have to deal with hygroscopic moisture, i.e. the water which condenses on the surfaces of all solids which are exposed to a moist atmosphere; with the water which adheres to the outside of bodies when they are separated from liquids, as by filtration; with water of crystallization; and, less frequently, with so-called *water of constitution*, or chemically combined water. In all of these cases the desiccation is effected by means of drying agents or by heat, or by means of both drying agents and heat.

To desiccate a substance by means of a drying agent, it is placed with the absorbent in a closed vessel (a desiccator), care being taken to provide for the greatest possible freedom of diffusion between them. Since the evaporation of the water upon or within the substance to be dried must precede its absorption, anything which promotes its volatilization is of advantage.

* It is unfortunate that we have not, at the present time, a more extensive and systematic knowledge of the aqueous vapor tension exerted at different temperatures by substances containing water, whether of crystallization or of constitution, and by aqueous solutions of varying concentration, since such knowledge, aside from its value in other directions, would be of the greatest utility in many quantitative operations.

Hence desiccators are often attached to filter pumps for the purpose of diminishing the pressure within them. Sometimes, with the same end in view, they are heated. This is permissible in some cases but not in all. If the absorbent, like calcium chloride, has a considerable vapor tension of its own at elevated temperatures, the desiccators must be kept cool. The drying agents which are commonly employed in desiccators are those that were mentioned in connection with the drying of gases, such as calcium chloride, sulphuric acid, and phosphorus pentoxide; and since there is no essential difference between the drying of a gas when it is passed over an absorbent and the drying of a solid when it is inclosed with the absorbent in a desiccator, whatever was said of them in the former connection is equally applicable to them in the latter. It may, however, be well to recall one caution, namely, that when sulphuric acid is used as a drying agent, care must be taken to exclude organic matter and all other substances which act upon it with formation of sulphur dioxide.

The evaporation of liquids at temperatures below their boiling points is greatly facilitated by constantly replacing the saturated atmosphere about them by one which is unsaturated with the vapor of the liquids. This principle can often be utilized with great advantage, not only in the evaporation of masses of liquids, but also in the desiccation of solids both at ordinary and at more elevated temperatures. The most efficient of all desiccators is one through which a current of dry gas, e.g. air, is passing. Conditions which retard the diffusion of the water vapor away from the drying materials should, of course, be avoided. For this reason substances to be dried, like liquids to be evaporated, should be placed in shallow vessels rather than in those with high sides. It will be seen, too, that advantage is to be gained by increasing the area of the evaporation, i.e. by spreading the material to be desiccated.

The removal of liquids from the surfaces of solids by evaporation, as in the drying of precipitates, is much slower at any

given temperature than could be anticipated from the known volatility of the liquids at that temperature. This is due to the fact that the vapor tension of a liquid, when in the form of a film upon the surface of a solid, is less at a given temperature than in other situations; also, in many instances, to the fact that such films are, in reality, concentrated solutions of the material of the solids which they surround. It is therefore well, if practicable, when a wet substance is to be rapidly dried, to heat it to a temperature several degrees above the boiling point of the liquid to be removed.

Hot-Air Baths

The ordinary rectangular copper hot-air bath is too familiar an object in the laboratory to require description. This form of bath, though convenient and in universal use, is sometimes unsuited to the drying of materials, owing to the readiness with which it is entered by the products of combustion from the lamp beneath. In this respect the cylindrical bath with its tight bottom and removable cover is superior to the usual form.

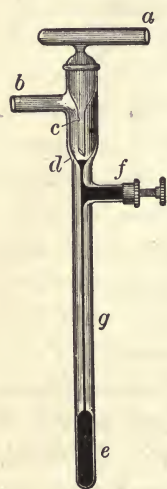


FIG. 40

The maintenance of constant temperatures in baths is a matter of great importance, and a large number of automatic gas regulators have been devised for this purpose. The best of these for general use is probably the Reichert regulator shown in Fig. 40. The gas enters the hollow stopper at *a* and passes through *b* to the lamp under the bath, one portion escaping from the stopper through the small hole *c*, and the remainder through the lower contracted end *d*. The hole *c* is so related to the outer wall that the flow of gas through it may be regulated, but not entirely stopped, by turning the stopper to the right or to the left. The flow through *d*, on the other hand, may be entirely cut off by the expansion of

the mercury in the bulb *e*. The instrument is provided with a side tube and a screw *f*, by means of which the column of mercury in *g* can be brought to any desired height. The adjustment of the instrument for the maintenance of any desired temperature is effected in the following manner: The screw *f* is turned to the right until the mercury rises and closes the passage *d*; the flow of gas through *c* is then regulated by turning the stopcock to the right or left until a flame is produced which will give to the bath, under all probable changes in the pressure on the gas supply, a temperature somewhat below that required. The screw *f* is now turned to the left, and gas is allowed to flow through *d* until the thermometer in the bath indicates that the desired temperature has been reached. The flow of gas through *d* is then stopped by turning the screw to the right. This first regulation of the temperature of the bath is never exact, and must be followed by repeated slight readjustments of the mercury by means of the screw.

The Reichert regulator will enable one to maintain in an ordinary bath, favorably situated as regards external conditions, a temperature which will not vary more than one or two degrees. The sensitiveness of the instrument, however, varies according to the capacity of the mercury bulb and the size and position of the outlet *d*. The hole through *d* should be quite small and should be located just above the point where the tube through which the mercury rises begins to expand into the larger chamber above. Many of the instruments are of faulty construction in these particulars, but a defective regulator may be rendered serviceable by removing the glass stopper and replacing it by a cork through which is passed a small glass tube drawn out to a fine point. But in this case special provision must be made for the portion of the gas supply which is ordinarily furnished through *c* by inserting Y-tubes in the rubber tubes leading to and from the regulator and controlling the flow of gas through the branch by means of a screw-pinchcock. Owing to the presence of sulphur in the gas, the mercury and the glass surfaces

in the vicinity of *d* become fouled with a black deposit which diminishes the sensitiveness of the instrument. This difficulty may be almost wholly overcome by passing the gas, before it reaches the regulator, over the surface of a concentrated solution of litharge in caustic soda. A good arrangement for the purpose is a flask in which the tube through which the gas enters or leaves is made to end just above the surface of the solution, but not quite in contact with it.

Another very excellent method of securing constant temperatures is by means of baths heated by the vapors of boiling liquids. The principle of this method is often employed in quantitative operations, as, for example, in the Hofmann and the Meyer methods of determining molecular weights, and in the heating of substances in tubes surrounded by the vapors of boiling liquids.



FIG. 41

In the bath of Victor Meyer, represented in Fig. 41, which is designed to take the place of the ordinary hot-air bath, the temperature is maintained by boiling a liquid. The quantity of liquid required is very small, as is also the consumption of gas. The boiling of the liquid is so regulated that the vapors condense in the lower half of the glass tube *a*. The temperature which will thus be reached and maintained in the bath is quite constant, but is usually a few degrees below the boiling point of the liquid. The condenser *a* may be replaced by an ordinary cold-water condenser, in which case the liquid can be boiled more rapidly in order to secure a temperature in the bath which is only slightly below the boiling point of the liquid. The ventilation of the bath is through the tube *b* and the small pivoted cover *c*. It will be seen that this arrangement permits the entrance into the bath of the products of combustion from the burner beneath. It may therefore be necessary, at times, to close *b* and to provide for ventilation by inserting a cork in the

cover through which are passed two tubes, one reaching nearly to the bottom, while the other ends near the top of the bath.

The constancy of the temperature which it is practicable to maintain in a bath depends very much upon external conditions, i.e. upon the fluctuations in the temperature of the air surrounding it. It is therefore well, whenever practicable, to surround the bath with nonconducting materials, and to protect it from air draughts by means of screens, or by placing it in a wooden box open on one side only.

As a rule, metallic baths should be covered with asbestos paper except at the place where the flame is applied. A permanently adhering cover may be readily obtained by laying the paper, thoroughly wet, upon the metallic surface and manipulating it with the hands until all of the air beneath has been driven to the edges and expelled.

Liquid Baths

It is often convenient in desiccating substances and for many other purposes to employ water or other liquid baths rather than the ordinary hot-air bath. Under suitable conditions a very satisfactory constancy of temperature can be maintained in such baths. A good thermo-regulator, like the Reichert, is as effective in a liquid as in a hot-air bath, and external protection by means of screens and nonconducting coverings is as advantageous to the former as to the latter. In general, the quantity of liquid in a water bath which is to be heated to a temperature below 100° should be as large as it is practicable to make it, and the lower the temperature to be maintained, the larger should be the vessel selected for the bath. Moreover, when the temperature to be secured is below the boiling point, the water in the bath requires constant agitation. A very effective arrangement for this purpose is a stirrer of sheet metal cut and bent to resemble a ship's propeller and attached to a vertical shaft which is rotated by a small electric, hot-air, or water



motor. In many cases a sufficient amount of agitation may be secured in the manner recommended by Ostwald, who employs an arrangement similar to a windmill, which is attached in a horizontal position to the upper end of the shaft and kept in motion by placing a burning lamp beneath. Since the amount of power obtained in this way is very small, the agitator must be constructed of light materials throughout, and pains must be taken to reduce as much as possible the friction upon the wearing parts. The arms of the windmill may be made of aluminium, or of wire bent into the proper form and covered with paper. As a means of propulsion, a small water air blast is more efficient than a lamp.

4. PRECIPITATION

Some judgment must be exercised with respect to the concentration of solutions from which precipitations are to be made. The fact that nearly all precipitates, especially when they are first formed, are somewhat soluble in their mother liquors suggests the propriety of avoiding unnecessary dilution previous to precipitation. On the other hand, it should not be forgotten that a moderate degree of dilution is advantageous and, in many cases, necessary. Rapidly forming precipitates inclose portions of the adjacent liquid and protect them, for a time at least, from the action of the precipitating agent. It is obvious that the incompleteness of the precipitation due to this cause, and also the slowness with which the precipitation will be completed in consequence of diffusion through the protecting layers of precipitated material, must increase with the concentration of the solution. It is obvious, too, that precipitates which inclose concentrated mother liquors must be difficult to cleanse by subsequent washing upon filters.

It is always necessary to add an excess of the precipitating agent, and the more soluble the precipitate, the larger should be the excess of the precipitant. If a solution of any silver

salt, e.g. silver nitrate, is mingled with one containing an exactly equivalent quantity of a chloride, e.g. sodium chloride, and the resulting silver chloride is separated from the liquid by filtration, the filtrate, though perfectly clear, will be found to contain both silver and chlorine; for if it is divided into two parts, and silver nitrate is added to one and sodium chloride to the other, both portions will give precipitates of silver chloride. Again, if a solution of any barium salt, e.g. the chloride, and one of any sulphate, e.g. sulphuric acid, are brought together in equivalent quantities and the precipitated barium sulphate is removed by filtration, the filtrate will give a further precipitation of sulphate when treated either with barium chloride or with sulphuric acid. It is not necessary, in order to obtain the further precipitation, to employ silver nitrate or sodium chloride in the first case, and barium chloride or sulphuric acid in the second. Any soluble silver salt or soluble chloride in the one instance, and any soluble barium salt or soluble sulphate in the other, will produce the same result. In other words, it is necessary only that the substance added and the precipitate shall have a constituent (ion) in common. This principle is of great utility in quantitative separations by precipitation.

Most precipitates, when first formed, are so finely divided that portions of them remain suspended for a time in the mother liquors. If immediate filtration is attempted, the filters become clogged and frequently cloudy filtrates are obtained. On standing, in contact with the mother liquors, the finer particles disappear while the larger ones grow to greater size; that is, the precipitates become coarser in time and therefore much easier to filter and to cleanse by washing. The change in a precipitate from the finer to the coarser condition is greatly facilitated by heat. These observations have given rise to the following rules: (1) Whenever practicable, precipitate from hot solutions; (2) continue to heat for some time after precipitation; (3) never attempt to filter until the supernatant liquid has become perfectly clear.

5. FILTERS

The filter paper which is now in common use for quantitative purposes, known as the *ashless* paper, consists almost entirely of cellulose and leaves a scarcely weighable residue when burned. It differs from the paper formerly used in that, in addition to a treatment with hydrochloric acid for the purpose of extracting inorganic bases, it has been subjected to the action of hydrofluoric acid for the purpose of eliminating silicic acid. These filters can be employed with safety without further purification and the weight of the ash may usually be neglected. If other filter papers must be employed, they should be cleansed and the ash which they leave when burned should be determined. To purify them, they are soaked, a large number at a time — from 24 to 48 hours, in quite dilute hydrochloric acid, and then washed with distilled water until the washings give no reaction for chlorine with silver nitrate. Owing to their tenderness while wet, some care must be exercised in manipulating them, or they will be torn and more or less disintegrated. To determine the ash, a number of the papers (from 5 to 15) are completely incinerated in a weighed platinum crucible and the weight of the residue ascertained.

A filter paper should be carefully fitted to the walls of its funnel at all points. This is easily accomplished if the walls of the funnel make the correct angle with its axis. The paper is folded symmetrically, opened in the funnel, and formed, as well as may be, to the sides. It is then wet with distilled water, allowed to drain, and again fitted to the sides of the funnel, care being taken not to rend the paper by rough handling. If the funnel is not of correct form, the last folding of the paper is made somewhat unsymmetrically, and the longer or shorter side is opened according as the angle of the sides is too great or too small. The funnels selected for papers of given sizes should be only slightly larger than the folded filters, since when the edges of the funnels are high above those of the papers, it is

much more difficult to introduce without loss the materials to be filtered and the liquids which are employed in washing the precipitates.

In filtering under diminished pressure, the portion of the paper which extends into the stem of the funnel requires support. The platinum cones devised by Bunsen are usually employed for this purpose. They are made in the following manner: A disk of platinum foil is cut in the form represented in Fig. 42, and a mold for it is made by allowing plaster of Paris to harden about the steel cone-model represented in Fig. 43.



FIG. 42

The platinum disk is softened in the flame, wrapped about the apex of the steel model, and then formed in the gypsum mold. If the platinum cone opens when removed from the mold, it is made a little too small by pressing the opposite sides with the fingers; it is then grasped with the forceps, reheated, and again formed in the mold. When finished it should perfectly maintain its shape and present no visible opening at the apex. If greater firmness is desired, the overlapping edges may be soldered at a single point by melting at the proper place a little borax and a fragment of gold. Any change in form due to the last operation is easily remedied by reshaping the cone in the mold. Instead of a platinum cone, one made by folding a small disk of the so-called *hardened* paper may be used to support the apex of the filter.



FIG. 43

The Gooch filter, which is often used with advantage in quantitative work, requires a platinum crucible, in the bottom of which a considerable number of minute holes have been made. The sides of the crucible are straight, and the bottom, which is flat, is provided with a closely fitting platinum cap, which is removed for filtering and replaced when the crucible and its contents are to be heated. The filter proper is made by depositing upon the perforated bottom of the crucible a layer of finely divided asbestos. The depth of the

layer and also the fineness of the asbestos used in making it may vary somewhat according to the coarseness of the material to be filtered.

To prepare the asbestos for use in this filter, a quantity of the material, of good quality, is macerated with water in a porcelain mortar until it is reduced to a sufficiently fine condition. It is then stirred up in a larger quantity of water and the portion which remains suspended for some time after the water has come to rest is floated out. The residue is soaked for several hours in moderately strong hydrochloric acid, filtered, washed with distilled water, dried, and finally ignited in a platinum dish over the blast lamp.

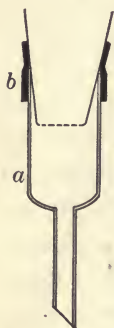


FIG. 44

In addition to the perforated crucible and the prepared asbestos, there are required for the completion of the Gooch filter the cylindrical glass funnel *a*, Fig. 44, and the rubber band *b* which serves to hold the crucible in place.

When a filter is to be made, a quantity of the prepared asbestos suspended in water is introduced into the crucible (arranged as shown in the figure), and the water is drawn off under moderately diminished pressure. Other portions of asbestos are afterwards introduced and treated in the same manner until a filter of sufficient thickness has been obtained. Finally, the filter is washed two or three times with water (to remove any material which would be likely to become dislodged and lost in subsequent operations), dried, and heated to constant weight at the temperature to which the precipitate which it is proposed to collect upon it is to be heated. It sometimes happens, during the collection and washing of a precipitate upon an asbestos filter, that some of the shreds of the filter are carried into the filtrate; the latter should always, therefore, be examined. If it is found to contain fragments of asbestos, these should be collected upon a filter of ashless paper and the loss to the filter determined by burning the paper and weighing the residue.

An asbestos filter which is of service in some cases is prepared by placing a perforated porcelain disk in the bottom of a cylindrical funnel, similar to that represented in Fig. 44, and depositing upon it a layer of prepared asbestos in the same manner as in making the Gooch filter.

The Monroe filter, which may often be used with advantage as a substitute for one of asbestos, is made in the following manner: A perforated Gooch crucible is placed upon filter or blotting paper and its bottom covered to a depth of 4 or 5 mm. with moist ammonium-platinum chloride. The crucible is cleansed externally, dried, covered, and placed in its cap. The double salt is then gradually decomposed by heat. If cracks appear in the filter, as they are likely to do, they are filled with a fresh portion of the double salt and the crucible is again heated. Finally, the upper surface of the filter of spongy platinum is made smooth by gently rubbing it with the end of a glass rod which has been rounded in the flame. All precipitates which can be dissolved in any reagent which does not attack platinum may be collected and washed upon such a filter. There is one danger, however, which is not to be overlooked. If the pores of the filter are filled with air, and a liquid containing free hydrochloric acid is passed through it, a little platinum will be dissolved.

6. FILTRATION

Liquids are filtered while hot, if practicable, because in that condition they pass through the filters much more rapidly than when cold. In quantitative separations, however, it is necessary to take into account the effect of temperature upon the solubility of the material to be collected on the filters.

In transferring a liquid and precipitate to a filter, it is best to introduce the greater portion of the former as free from the latter as may be; in other words, it is well not to stir up the precipitate unnecessarily until nearly all of the liquid has been passed through the filter. The purpose of this is, of course, to

postpone as long as possible the clogging of the filter which is sure to follow the introduction of a finely divided precipitate. When only a little of the liquid remains with the precipitate, the latter is stirred up and as much of it as possible is introduced into the filter with the residue of the former. A small quantity of the filtrate — always less than a filterful — is then returned to the vessel and more of the precipitate is brought upon the filter in the same manner. This procedure is repeated until but little of the precipitate remains except that which is attached to the sides and bottom of the vessel. To complete the transference of the precipitate, a small quantity of the filtrate (3 to 5 cc.) is poured into the vessel and the whole interior surface is washed down with a feather or with a rubber on the end of a glass rod. The detached material is then stirred up with the liquid and brought upon the filter. This last operation must be repeated until no particles of the precipitate can be detected upon the sides or bottom of the vessel, and until the wash liquid is entirely free from any appearance of cloudiness.

There are two good reasons for the practice of employing the filtrate, rather than water or some other liquid, to bring the precipitate upon the filter. In the first place, the filtrate, being already saturated, exerts no solvent action on the precipitate; in the second place, the volume of the filtrate is not increased by its use for this purpose as it would be if another liquid were employed.

To prepare a feather for use in detaching precipitates from the interior surfaces of vessels, it is trimmed in the following manner: At a point near the free end — where the rachis is judged to be sufficiently stiff and elastic — the feather is cut off transversely at an angle of about 30° to its axis. The barbs on either side are then cut away for a distance of about 15 mm. in lines parallel to the rachis and at a distance of 2–4 mm. from it. The remainder of the rachis is entirely denuded of barbs and made very smooth by scraping with the edge of a sharp knife blade.

A substitute for the feather, which is in common use, is familiarly designated as the "policeman." It is made from a rectangular piece of sheet rubber by covering one side — except a narrow strip through the center — with cement and then once folding the piece through the middle at right angles to the uncovered strip. A long pocket is thus provided, into which the end of a glass rod may be crowded. This arrangement, though not superior to the feather, is to be preferred to a glass rod with a short piece of rubber tubing drawn over the end, which is sometimes used in cleansing beakers, since the uncovered condition of the end of the rod in the latter affords the precipitate an opportunity to become lodged between the rubber and the glass.

7. THE WASHING OF PRECIPITATES

It is important that the washing of precipitates should be accomplished with the least possible quantity of liquid: 1st, because of the solvent action of the wash liquid upon the precipitate; 2d, in order to avoid an unnecessary increase in the volume of the filtrate; and 3d, for the purpose of saving time. To this end the filter pump, or some other means of securing diminished pressure, should always be employed in the washing of precipitates, and before introducing a fresh portion of the wash liquid as much of the liquid already in the filter should be withdrawn as it is possible to extract with its aid. How irrational a different course would be will appear from the following illustration. We will suppose that in washing a given precipitate 25-cc. portions of water are introduced into the filter, and that after each addition all but 0.5 cc. is withdrawn with the aid of the pump. Theoretically the impurities would be reduced by the first washing to 0.02; by the second, to 0.00039; by the third, to 0.0000077; and by the fourth, to 0.00000015. Suppose, on the other hand, that the successive 25-cc. portions of water are added while 5 cc. of liquid remain in the filter. Theoretically the impurities will then be reduced by the first

washing to 0.2; by the second, to 0.0333; by the third, to 0.00556; and by the fourth, to 0.000926. A comparison of the two sets of figures will convince one of the immense advantage to be gained in washing precipitates by drawing off, as completely as possible, the liquid already in a filter before adding a fresh portion of the wash liquid.

The above estimate of the rate at which the impurities will be reduced under the given conditions is based on the supposition that when a quantity of wash liquid is introduced into the filter, the impurities will distribute themselves uniformly through the whole body of the liquid, and that the portion which passes through the filter into the filtrate is therefore of the same concentration as that which remains behind in immediate contact with the precipitate and the material of the filter. As a matter of fact, however, the portion of the solution which remains behind and cannot be extracted by the pump is always more concentrated than the filtrate. It is for this reason that the cleansing of a precipitate by washing is found in practice—even under the best management—to be much slower than is indicated by the computations just given. Nevertheless, the argument in favor of thoroughly extracting the liquid already in a filter before introducing a fresh portion of the wash liquid holds good.

The tendency of solutions to become more concentrated in the immediate vicinity of solids, e.g. around precipitates and the material of filters, is known as *adsorption*. A familiar effect of adsorption is that which is observed when a standard solution is passed through a dry filter; the first portion of the filtrate is well known to be weaker than the original solution, and it is therefore always rejected.

Precipitates which—owing to their fine state of subdivision—work themselves into the interstices of the filter and clog it to such an extent as seriously to interfere with filtration are often partially washed by decantation before bringing them upon the filter; that is, they are stirred up with portions of the

wash liquid, which, when the precipitates have subsided, are poured into the filter. This method of cleansing precipitates is, however, exceedingly ineffective, owing to the large fraction of the liquid which must each time be left with the precipitate. The objection to it is identical with that to the practice of introducing wash liquid into filters before removing as much as possible of the liquid already in them.

It has been stated that if a saturated solution of a compound is treated with a soluble substance containing one of the constituents into which the compound dissociates in solution, some of the dissolved material will be precipitated, and that, for this reason, it is customary to add an excess of the precipitating agent. The same principle may be utilized with great advantage at times to diminish the solubility of precipitates in the liquids with which they are washed; for example, if a precipitate of barium chromate is to be washed with water containing a little acetic acid or an acetate in which it is sensibly soluble, its solution may be almost entirely prevented by adding a little ammonium chromate to the wash liquid. The quantity of the salt required for this purpose is very small, and when the other impurities have been washed out of the precipitate the little ammonium chromate introduced with the wash liquid may be sufficiently eliminated by a very moderate washing in pure water in which barium chromate is only slightly soluble.

If freshly precipitated silver chloride is collected upon a filter and is then washed for a long time with pure water — especially with cold water — it will be noticed that the filtrate remains perfectly clear as long as any of the liquid in which the precipitation was made is still in the filter, and for some time after the beginning of the washing with water; that later, however, the upper portions of the filtrate become cloudy from the presence of precipitated silver chloride. If the receiving vessel is exchanged for an empty one, and the washing with water is continued, a clear filtrate will be obtained, which, nevertheless, becomes cloudy when any acid or soluble salt is added to it. On

the other hand, if a little acid or a small quantity of some salt is added to the water before beginning the washing of the precipitate, the filtrate will remain clear to the end. The explanation of this conduct is as follows: Silver chloride, when freshly precipitated, belongs to a class of bodies known as *colloids*, a characteristic of which is the tendency to form with pure water so-called pseudo solutions, from which they are reprecipitated by the addition of acids or salts. The solution of the silver chloride, therefore, does not begin, in the case just cited, until these substances have been removed from the filter by washing, and a reprecipitation follows because of their presence in the filtrate. Familiar examples of precipitates which behave in a similar manner are the hydroxides of iron and aluminium and the sulphides of the metals. Such substances are difficult to cleanse by washing, owing to their voluminous and sometimes gelatinous character and their tendency to clog the filters. On standing and when heated, they usually become more compact and therefore easier to wash upon filters. In the more compact condition they are also less inclined to redissolve—to “run through” the filter—on continued washing. In dealing with them it is well to precipitate from hot solutions and to keep the liquid hot for some time after precipitation; to allow them to stand a long time before attempting filtration; and to add to the wash water some substance which will prevent a return to the pseudo-soluble condition. It appears to make but little difference what substance is employed for the last purpose so long as it does not affect the composition of the precipitate; it is therefore well, when permissible, to select ammonium salts, since these can afterwards be expelled from the precipitates by heat.

CHAPTER IX

SILVER AND THE HALOGENS

EXERCISE XVI

DETERMINATION OF CHLORINE AND SILVER

I. GRAVIMETRICALLY AS SILVER CHLORIDE

Weigh into a beaker—preferably one having a “lip”—about 0.2 gram of pure potassium chloride. Dissolve the salt in 75 or 100 cc. of water and add slowly, with constant stirring, a dilute solution of silver nitrate, to which have been added a few drops of nitric acid, until it is believed that the silver nitrate is slightly in excess. Let the precipitate subside and then add to the nearly clear supernatant liquid a little more of the silver nitrate. If the cloudiness does not increase, warm the contents of the beaker for half an hour upon a sand bath or a wire gauze, stirring vigorously from time to time, and then set the beaker aside in a dark place.

When the liquid above the precipitate has become perfectly clear, rub the under side of the beaker lip with a minute quantity of vaseline or with some kind of grease. This is intended to prevent the liquid from working its way over the edge and running down the outside of the beaker while being transferred to the filter. The precaution, though customary, is hardly necessary, since with proper manipulation there is no need of loss from this cause. Bring the precipitate upon a small ashless filter which is arranged for use with the filter pump.

In transferring the contents of the beaker to the filter, a glass rod is held vertically with its lower end reaching nearly to the

bottom of the filter, and against this is laid the edge of the beaker at the point over which the liquid and precipitate are to pass. In this way the liquid is made to glide quietly down the rod and enter the filter without spattering. When the filter has been sufficiently filled, the beaker is tilted backwards, but the rod should not be removed as long as any liquid remains between it and the edge. If a little becomes lodged at the point of contact, as is usually the case, it may be made to flow in the one direction or the other by changing the angle of the rod and by sliding it up and down over the edge of the beaker. If the rod is removed prematurely, the liquid and precipitate which are entangled between it and the beaker will run over the edge and down the outside of the latter; and when the outside has once become wet, it is difficult to avoid a repetition of the accident.

The precipitate which adheres to the beaker is brought into the filter with the aid of small portions of the filtrate and a trimmed feather or a "flag," as described in the preceding chapter.

To wash the precipitate, first remove the mother liquor as completely as possible with the aid of the filter pump, and then, after having detached the pump, moisten the precipitate and paper with a small quantity of cold water containing a little silver nitrate. Give the impurities to be removed by the washing a little time for diffusion, and then, as before, draw off the liquid with the pump as completely as possible. Continue washing the precipitate in this manner with water containing silver nitrate until the potassium nitrate has been removed, and then wash it two or three times in the same way with small portions of cold water containing a very little nitric acid. The silver nitrate is added to the first wash water to diminish the solubility of the silver chloride and also to prevent its return to the colloidal condition. The nitric acid in the water which is employed in the last stage of the washing process does not directly affect the solubility of the chloride, but it effectually corrects the tendency to revert to the colloidal state.

Dry the filter at 100° or slightly above that temperature. Open it on a piece of glazed paper and transfer the silver chloride to a weighed porcelain crucible which is also placed upon the paper. If necessary, a piece of stiff platinum wire or a small platinum spatula may be employed to detach the chloride which adheres to the paper, in which case the wire or spatula is afterwards to be wiped clean upon the paper. Fold the paper in the form of a square by turning in the edges, and roll it together tightly, but in such a way that the half of the paper which has been in contact with the precipitate is all at one end. Beginning in the middle of the roll, wind a platinum wire spirally about the half which contains no chloride. The wire should be so long that about 75 mm. of its length will not be required in the winding. With the unused end of the wire in one hand, hold the roll over the crucible in a vertical position with the free end upward, and with a lamp—burning with a small but good oxidizing flame—in the other hand light it at the top. If, as the flame descends, portions of the paper are incompletely burned, touch the parts which are only charred with the edge of the flame as often as may be necessary to complete the incineration. When the roll has been completely burned down to the point where the wire begins, turn it into a horizontal position and burn the part inclosed by the wire. It is important that no incompletely burned matter should drop from the wire, since the combustion cannot be finished in the crucible. The roll must therefore be held very steadily, and to this end it is well to support the hand by resting it on the table or on a block. If the column of ash outside of the wire curls over and appears to be in danger of breaking off and falling before the burning is completed, its position should be so changed as to diminish the strain. Transfer to the crucible anything which may have fallen upon the glazed paper, add a few drops of dilute nitric acid, and evaporate it at a very moderate temperature. Repeat the treatment with nitric acid and the evaporation, and then add a few drops of hydrochloric acid.

Evaporate to dryness and heat the crucible until the chloride in it begins to fuse around the edges. Cool the crucible in a desiccator and weigh. To remove the chloride from the crucible, introduce a piece of zinc and a little hydrochloric or sulphuric acid.

Silver chloride melts at about 450° . It is perceptibly soluble even in cold water, but less so, as explained already, in water containing a small quantity either of a soluble silver salt or of a chloride. The presence of a considerable quantity of chlorides or of the nitrates of the metals of the alkalies and alkaline earths increases its solubility. It is easily dissolved in solutions of potassium cyanide, sodium thiosulphate, and ammonia.

The method just given suffices in the case of most soluble chlorides for the separation of chlorine from the metals. Stannic, mercuric, antimony, platinic, and chromic chlorides are exceptions to the rule. In solutions of the first four, silver nitrate precipitates, in addition to the chlorine, some of the metal with which it was previously combined. In solutions of chromic chloride the precipitation is incomplete. The determination of chlorine in these salts must be preceded by a separation of the metals. The tin is best precipitated by ammonium nitrate; the antimony and mercury, by hydrogen sulphide; and the chromium, by ammonia. Solutions of platinic chloride are evaporated to dryness with sodium carbonate and the residue is heated to the fusing point in a platinum crucible. The sulphides of some of the metals, when precipitated from solutions of their chlorides by hydrogen sulphide, are inclined to carry down with them a portion of the chlorine. In such cases the solution should be dilute and fully saturated with the gas. It should also be allowed to stand for some time after saturation in a closed vessel before filtration. If practicable, the sulphide should be redissolved and again precipitated.

Lead, silver, and mercurous chlorides, because of their insolubility, also require special preliminary treatment. The first is

decomposed by digestion with acid sodium or potassium carbonate; the second, by fusion with an alkaline carbonate; and the third, by digestion with caustic soda or potash.

Bromine and iodine are determined as silver salts in the same manner as chlorine. Care must be taken, however, not to treat solutions of their salts with nitric acid until after an excess of silver nitrate has been added. This precaution is especially necessary in the case of the iodides, which, with the exception of silver iodide, are quite readily decomposed by nitric acid with liberation of iodine.

Bromine and iodine are separated from the various metals by the same methods as chlorine. There are also certain special methods which may be employed to separate iodine from some of the metals.

To determine silver as chloride, the solution containing it is treated, at a temperature somewhat below the boiling point, with a few drops of nitric acid and then with a very moderate excess of hydrochloric acid, or of sodium or potassium chloride. The precipitate is washed on the filter, first with cold water containing a little nitric acid, and then two or three times with pure water. In all other respects the procedure is the same as in the determination of chlorine.

It is customary to state the results of quantitative determinations in the form of percentages, not of the constituents determined, but of the whole material or compound employed in the analysis; for example, the result of a determination of chlorine in potassium chloride would be expressed as follows:

Theoretical percentage of Cl in KCl =	47.53
Found " " " " " =	
Error =	 per cent.

If the quality of the work is to be judged, it is fairer to state the results in the form of weights, as follows :

Theoretical weight of Cl in	gram.	KCl = ...	gram.
Found	" " " " " "	" " " "	" "
			Error = <u> </u> "

It will be seen that when the results are expressed in the customary form, the effect of the algebraic sum of the errors of the analysis is inversely proportional to the quantity of the material operated upon. In other words, if large quantities of material are employed, one may work somewhat carelessly and nevertheless obtain seemingly good results. This fact is of course a strong argument in favor of using only small quantities. Another sufficient reason for the employment of only moderate quantities of material is to be found in the fact that small precipitates are much more easily and rapidly cleansed by washing than large ones.

Much of the time which is usually spent in making computations may be saved by preparing, before beginning a piece of quantitative work, a table of equivalent weights which includes all of the substances involved in the calculations to be made. A table of this kind including nearly all the substances employed in the present chapter will be found on the following page. In the horizontal lines are given the quantities of various substances which are equivalent to unit quantities of the substances designated in the first vertical column. They are found, of course, by dividing the atomic or molecular weights — or the proper multiples of them — of the substances whose symbols stand at the head of the several columns by the atomic or molecular weights of those whose symbols are given in the first column. For example, to find the weight of bromine which is equivalent to any unit weight of chlorine, we divide 79.35, the atomic weight of the former, by 35.18, the atomic weight of the latter, and obtain 2.2555, which is the number under Br

Atomic and Molecular Weights

Cl . . .	35.18	Ag . . .	107.11	AgCl . . .	142.29	CrO ₃	99.34
Br . . .	79.35	KCl . . .	74.00	AgBr . . .	186.46	K ₂ Cr ₂ O ₇ . . .	292.00
I . . .	125.89	KBr . . .	118.17	AgI	233.00		
K . . .	38.82	KI	164.71	As ₂ O ₃ . . .	196.54		

Table of Equivalent Weights

	Cl	Br	I	K	Ag	KCl	KBr	KI	AgCl	AgBr	AgI	As ₂ O ₃	CrO ₃	K ₂ Cr ₂ O ₇
Cl	1.0000	2.2555	3.5784	1.1034	3.0446	2.1034	3.3590	4.6816	4.0446	5.3002	6.6230	1.3966	0.9412	1.3833
Br	0.4433	1.0000	1.5865	0.4892	1.3498	0.9326	1.4892	2.0757	1.7932	2.3498	2.9363	0.6192	0.4169	0.6133
I	0.2794	0.6303	1.0000	0.3083	0.8508	0.5878	0.9387	1.3083	1.1302	1.4811	1.8508	0.3903	0.2630	0.3866
K	0.9062	2.0440	3.2429	1.0000	2.7591	1.9062	3.0440	4.2429	3.6653	4.8031	6.0020			
Ag	0.3284	0.7408	1.1753	0.3624	1.0000	0.6909	1.1032	1.5377	1.3284	1.7408	2.1753			
KCl	0.4754	1.0723	1.7012	0.5246	1.4473	1.0000	1.5959	2.2258	1.9228	2.5197	3.1486			
KBr	0.2977	0.6714	1.0653	0.3285	0.9064	0.6262	1.0000	1.3938	1.2041	1.5779	1.9717			
KI	0.2136	0.4817	0.7643	0.2358	0.6503	0.4492	0.7174	1.0000	0.8639	1.1320	1.4146			
AgCl	0.2472	0.5577	0.8847	0.2728	0.7527	0.5202	0.8305	1.1575	1.0000	1.3104	1.6375			
AgBr	0.1886	0.4255	0.6751	0.2082	0.5744	0.3969	0.6338	0.8833	0.7631	1.0000	1.2496			
AgI	0.1510	0.3406	0.5403	0.1666	0.4597	0.3176	0.5071	0.7069	0.6107	0.8002	1.0000			
As ₂ O ₃	0.7160	1.6149	2.5621									1.0000	0.6739	0.9904
CrO ₃	1.0624	2.3963	3.8018									1.4838	1.0000	1.4800
K ₂ Cr ₂ O ₇ . .	0.7228	1.6304	2.5867									1.0096	0.6804	1.0000

and opposite Cl in the table. Again, if $K_2Cr_2O_7$ acts upon an iodide in an acid solution, there are liberated six atoms of iodine for each molecule of the bichromate, and to find the weight of the former, which, in such a reaction, is equivalent to a unit weight of the latter, we divide six times the atomic weight of iodine (6×125.89) by 292, the molecular weight of the bichromate. The result is 2.5867, which is the number in the table under I and opposite $K_2Cr_2O_7$. The manner of using such a table is obvious, but its usefulness will be illustrated by a few examples. Suppose a quantity of potassium chloride, W , has been weighed out, and it is desired to know what weight of silver chloride it should yield, we find in the table opposite KCl and under AgCl the number 1.9228; the weight of the silver salt is $W \times 1.9228$. Suppose a weight of silver chloride, W_1 , has been obtained, and we desire to find the weight of the chlorine in it; under Cl and opposite AgCl is given the equivalent 0.2472, and the weight of the chlorine is $W_1 \times 0.2472$. Suppose again that we have a given weight of arsenious oxide, W_{II} , and are required to ascertain how much potassium bichromate will be needed for its oxidation to arsenic acid; by referring to the table we find the weight to be $W_{II} \times 0.9904$.

II. VOLUMETRICALLY BY MOHR'S METHOD

One-tenth normal solutions of potassium chloride and of silver nitrate are required.

To prepare the former, weigh out about 7.5 grams of pure potassium chloride. The quantity must not be less than 7.4, and should not exceed 7.6 grams. Dissolve the salt and dilute the solution in a liter measuring flask to the mark on the neck. Divide the weight of the salt in solution by the capacity of the flask in cubic centimeters to find the amount of the salt in one cubic centimeter, and then divide 7.4, the weight of the salt in one liter of a tenth-normal solution, by the quotient. The second quotient will be the number of cubic centimeters of the

solution which must be diluted to one liter, and the difference between this and 1000 will be the volume of the water required for the dilution. Remove from the flask with a pipette a quantity of the solution which is somewhat greater than that of the water to be introduced. Measure in the required volume of water and fill the flask to the mark with the solution which was withdrawn. Close the flask and thoroughly mix its contents. The solution should have, at the time of its dilution, very nearly the standard temperature.

To prepare the solution of the silver salt, dissolve about 21 grams of neutral silver nitrate in 1200 cc. of water. Fill one burette with the tenth-normal potassium chloride solution, and another with the solution of silver nitrate. Measure into a beaker 10 cc. of the chloride solution. Add about 50 cc. of water and a few drops of a solution of neutral potassium chromate which is free from chlorine. The liquid in the beaker, after the addition of the chromate, should have a distinct but not a deep yellow color. Titrate the solution of the chloride, stirring it constantly, with the solution of silver nitrate until a slight but permanent red color is obtained. Repeat the experiment several times with fresh portions of the chloride. Having found the number of cubic centimeters of the silver solution which are equivalent to ten of the chloride, multiply by 100. The product will be the number which must be diluted to a liter. Measure the water required for the dilution into a dry liter flask, and fill to the mark with the solution of silver nitrate. The two solutions should be equivalent; determine whether they are so.

Weigh off from 0.1 to 0.2 gram of pure potassium chloride, and determine the chlorine in it by means of the standard solution of silver nitrate.

Barium and lead form nearly insoluble chromates; therefore to determine chlorine in combination with these metals it is necessary to add a slight excess of the chromate, — i.e. somewhat more than is required for their precipitation. The titration

may then be made without removal of the insoluble chromates. Or the metals may be precipitated as sulphates with sodium sulphate.

Silver chromate does not form in the presence of acids, and silver oxide is precipitated by the alkalies; hence all the solutions employed in connection with the method of Mohr must be neutral, and the presence of reducing substances is, of course, inadmissible.

Silver chromate is soluble in 6666 parts of water at 17.5° , and in 3704 parts at 100° ; if, therefore, potassium chromate is added to a solution of silver nitrate, a red precipitate is obtained, which disappears rather slowly on titrating with a solution of a chloride. For this reason it is not advisable, when silver is to be determined, to treat its solution with the chromate and then to titrate with a standard solution of some chloride until the red color is destroyed. It is much better to add at once an excess of the chloride, and then to determine the amount of the excess by means of a standard solution of silver nitrate.

Bromine and iodine may also be determined by the method of Mohr.

III. VOLUMETRICALLY BY VOLHARD'S METHOD

Dissolve about 10 grams of ammonium sulphocyanate in 1200 cc. of water. Fill one burette with the solution, and another with the tenth-normal solution of silver nitrate. Measure 10 cc. of the latter into a beaker. Add 5 cc. of a cold saturated solution of ferric ammonium sulphate and about 50 cc. of water. Stir in dilute nitric acid, drop by drop, until the solution becomes nearly colorless. Titrate with the solution of sulphocyanate until a faint but permanent red color appears. Repeat the experiment several times. Having found the relation of the two solutions, dilute that of the sulphocyanate to the tenth-normal standard, proceeding as directed under II.

If the ammonium sulphocyanate is quite wet at the time of weighing, the preliminary solution of it may be found to be too

weak; it is therefore well, in such a case, to weigh out somewhat more than the prescribed quantity of the salt. But if the required additional quantity has been considerably overestimated, giving a much too concentrated solution of the sulphocyanate, it should be diluted before making the determinations on which the final dilution to the standard is to be based. As a rule, solutions which are to be diluted to any fixed standard should have, at the time of determining their strength, very nearly their final concentration.

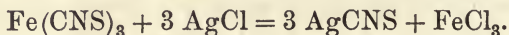
The nitric acid (specific gravity 1.2) which is used to decolorize the indicator should be boiled to free it from nitrous acid and oxides of nitrogen.

Dissolve a weighed silver ten-cent piece in dilute nitric acid and evaporate nearly all the excess of the acid. Dilute with water and boil the solution to remove nitrous acid and oxides of nitrogen. Pour the solution, when cold, into a 100-cc. measuring flask, add the washings, and dilute to the mark with water. Determine the silver in measured portions of the solution.

According to Volhard, silver may be determined in the presence of copper without difficulty provided the ratio of the latter to the former does not exceed that of 7 to 10. In the presence of nickel and cobalt the determination is satisfactory, but requires some practice. Mercury and palladium, on the other hand, must be removed before the silver can be estimated.

Weigh out from 0.1 to 0.2 gram of pure potassium chloride and dissolve it in about 100 cc. of water. Add 5 cc. of the iron solution and decolorize with nitric acid. Measure in an excess of the standard solution of silver nitrate — about twice the quantity required to precipitate the chlorine — and then titrate with the solution of sulphocyanate, stirring constantly, until the liquid assumes a light yellowish-brown color. The difference between the quantity of silver added in the first place and that found by the subsequent titration with the sulphocyanate is the quantity which was required to precipitate the chlorine.

The end-reaction when chlorine is determined in the manner prescribed above is much less striking than when silver is precipitated by sulphocyanate in the absence of silver chloride, and the color due to the formation of ferric sulphocyanate is not permanent if the excess of sulphocyanate is small. This is due to a reaction between the coloring substance and silver chloride:



A little experience, however, enables one to determine with ease and certainty when the precipitation of the silver is complete. It is well, when this method of determining chlorine is employed for the first time, to continue adding the sulphocyanate until a deep color is developed, and then to add silver nitrate until it is destroyed. A few such titrations, back and forth, in the same solution, with close observation of the changes in color, will prepare one sufficiently for accurate work. The difficulty resulting from the reaction between the ferric sulphocyanate and the silver chloride may be avoided in the following manner: The solution of the chloride, the indicator, and the excess of silver nitrate are placed in a small measuring flask and well shaken. The flask is filled to the mark with water, the contents thoroughly mixed, and then quickly filtered through a dry paper, the first portions of the filtrate being discarded. The excess of silver is then determined by titrating measured portions of the filtrate with the standard solution of sulphocyanate.

When the quantity of chlorine to be determined is not even approximately known, it is recommended to add a drop or two of the sulphocyanate solution from time to time while measuring in the silver nitrate. As long as any chlorine remains unprecipitated, the color produced by the sulphocyanate will disappear slowly, but when the silver is in excess, it disappears instantly. The quantity of sulphocyanate introduced in this way must, of course, be added to that which is subsequently used in determining the excess of silver.

When the silver is standardized in the manner prescribed under II, and afterwards used for the determination of chlorine by the method of Volhard, the results are, as a rule, somewhat low in consequence of the reaction between the ferric sulphocyanate and the silver chloride. It is therefore recommended that a solution of silver nitrate which is to be used principally for the estimation of chlorine by this method be especially standardized for chlorine. For this purpose a solution of a weighed quantity of a pure chloride is treated with the indicator and an excess of the preliminary solution of silver nitrate, and then titrated with any very dilute solution of ammonium sulphocyanate. Having found in this way the volume of the sulphocyanate solution required to precipitate the excess, the relation of the silver and sulphocyanate solutions to each other is ascertained. The difference between the volume of the silver nitrate added to the chloride and that found to be equivalent to the sulphocyanate which was used in precipitating the excess of silver is the volume of the silver nitrate which is equivalent to the weighed quantity of chloride. A solution which is standardized in this manner will give correct results when employed for the estimation of chlorine by the method of Volhard, but it must be restandardized as directed under II when the method of Mohr is to be used.

Bromine is determined by the method of Volhard in precisely the same manner as chlorine. The end-reaction, however, is more distinct and permanent, owing to the fact that silver bromide is decomposed by ferric sulphocyanate much more slowly than silver chloride.

To determine iodine, the iodide dissolved in two or three hundred times its weight of water is placed in a bottle having a ground-glass stopper. The silver nitrate is added in small quantities, and after each addition the bottle is closed and the contents are well shaken. This treatment is continued until

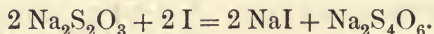
the silver iodide separates and leaves the supernatant liquid quite clear. A little more silver nitrate, also the indicator, and the nitric acid necessary to bleach it are then added, and the excess of the silver is determined with the sulphocyanate. But — since silver iodide carries down with it a quantity of silver nitrate, and the color indicating the end of the reaction is not permanent until the nitrate thus precipitated has all been converted into sulphocyanate — the standard solution of sulphocyanate must be added in small quantities and the contents of the bottle must be vigorously agitated after each addition.

The method of Volhard is usually preferred to that of Mohr for the reason that by it silver and the halogens may be determined in the presence of nitric acid and therefore in solutions containing substances which, in the absence of nitric acid, reduce the salts of silver.*

EXERCISE XVII

IODOMETRIC DETERMINATIONS

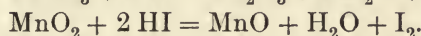
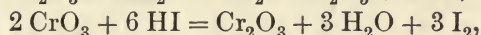
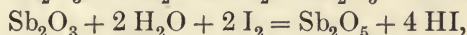
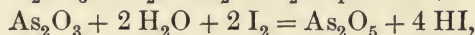
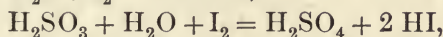
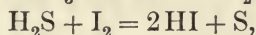
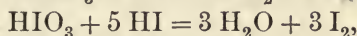
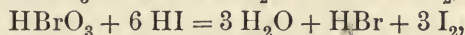
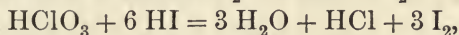
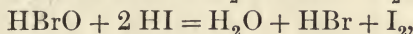
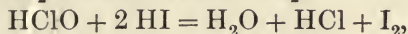
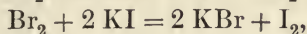
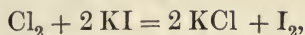
These are all based on the reaction which takes place between free iodine and sodium thiosulphate :



It will be seen that by the aid of this reaction it is practicable to determine all of those substances which liberate from iodides a definite quantity of iodine, and all of those also which convert into iodides, or absorb, a definite amount of free iodine. The following equations represent the reactions with iodine or the

* The student should also familiarize himself with the volumetric methods of Gay-Lussac, of Pisani, and of Bohlig. See Fresenius, *Quant. Analyse*, 1, 302, 309, 472.

compounds of iodine, of some of the substances which are determined by the iodometric method:



I. PREPARATION OF STANDARD SOLUTIONS

a. Resublimed Iodine

Select two crystallizing dishes of the same diameter whose edges fit together quite closely. Place in one of them a mixture of 10 or 15 grams of commercial iodine and 2 or 3 grams of pulverized potassium iodide. Press the dish halfway through a hole which has been made for it in a piece of asbestos board 150 or 200 mm. square, and bring under it a sand or asbestos bath which is narrower than the board. Heat the iodine slowly, allowing the vapors to escape until it is believed that all the water has been expelled, and then invert over it the other crystallizing dish. Distill the iodine very slowly, and keep the upper dish cool by placing upon it a flat-bottomed metallic dish containing cold water. When the sublimation is finished, transfer the iodine to a glass-stoppered weighing flask and place the latter in a desiccator. The purified iodine is used in standardizing thiosulphate solutions.

b. Potassium Iodide

Aqueous solutions of potassium iodide are employed as a solvent for free iodine and also as the source of the iodine which is liberated in various reactions utilized in iodometric processes.

The salt must be tested for the presence of iodate. For this purpose a small quantity of the iodide is dissolved in recently boiled water and treated with a little well-boiled dilute hydrochloric acid. If the solution remains colorless for a few minutes, it is free from iodates. Starch paste may be added to facilitate the detection of free iodine. Within a short time the solution will become colored in consequence of the action of the free oxygen in it on the hydriodic acid which is liberated by the hydrochloric acid. If the iodide is found to contain iodate, the latter may be removed by boiling the water solution of the salt with zinc amalgam until it no longer gives the reaction for iodic acid when treated with hydrochloric acid and starch paste. Neither zinc nor mercury is dissolved when a solution of an iodide is treated in this manner. The former is converted into hydroxide, which may be removed by filtering through a paper which has been thoroughly wet with boiling water.

c. Starch

Grind about one gram of arrowroot starch with a little water and pour the mixture into 150 or 200 cc. of boiling water. Continue to boil the liquid for about one minute, and then allow it to cool and settle. The clear portion only is to be used for the detection of free iodine. A new preparation of starch is to be made for each day's work.

d. The Solution of Iodine

To prepare this, measure into a liter flask a volume of potassium iodide solution which contains 18 grams of the salt. Weigh in a little over 13 grams of commercial iodine. Close

the flask and shake it until the iodine is dissolved. If the solution progresses too slowly, it may be hastened by adding more of the potassium iodide. Introduce 200 or 300 cc. of water and agitate again. Continue to add water and to agitate after each addition until the flask is filled to the mark, making sure that all of the iodine is dissolved.

e. The Solution of Sodium Thiosulphate

Weigh about 27.5 grams of the salt into a liter flask. Dissolve it in water and dilute to the mark.

f. Standardization of Solutions d and e

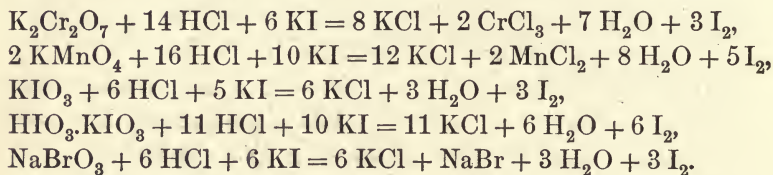
Fill one burette with the solution of thiosulphate and another with that of iodine. Measure 10 cc. of the former into a beaker. Dilute with water and add 1 or 2 cc. of the starch preparation. Titrate with the iodine solution, stirring constantly, until a faint blue color is developed which disappears on the addition of a very minute quantity of thiosulphate. Repeat the experiment until constant results are obtained.

Having found the relation of the iodine and thiosulphate solutions, it remains to determine the exact strength of the latter. To do this, measure about 10 cc. of a potassium iodide solution (10 : 1) into a glass-stoppered flask, and weigh in from 0.1 to 0.2 gram of the resublimed iodine. Close the flask and shake it until the iodine is dissolved. Add a little water, then close the flask and shake it again. Proceed in this way until a solution is obtained which is so dilute that no vapors of iodine can be seen above it. Add now the thiosulphate until the color of the solution has nearly disappeared, and then 1 or 2 cc. of the starch. Add thiosulphate again until the solution becomes quite colorless, noting carefully, however, the quantity required just to destroy the blue color. From another burette add the iodine solution *d* until a faint blue color appears.

Subtract from the total volume of the thiosulphate used the quantity equivalent to the iodine solution *d* which was used to restore the blue color. The difference is the volume of the thiosulphate which is equivalent to the known weight of pure iodine. Repeat the experiment with another weighed portion of iodine. Having found the strength of the thiosulphate solution, and indirectly that of the iodine, the two solutions may be diluted to any desired standard. One-tenth normal solutions are usually employed, though it is often advantageous to dilute to one-half and even to one-tenth of that strength.

Neither solution is stable, and both require frequent restandardization. They lose strength less rapidly when kept in a cool, dark place.

It has been proposed to employ for the restandardization of the thiosulphate standard solutions or weighed quantities of stable compounds which, when acidified, in the presence of potassium iodide, liberate a definite quantity of iodine. The following equations represent some of the reactions which have been utilized in this way:



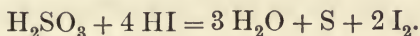
II. IODOMETRIC DETERMINATION OF SULPHUROUS ACID

Weigh about 5 grams of sodium sulphite into a half-liter measuring flask. Dissolve the salt in water and dilute to the mark. Measure 10 cc. of the standard solution of iodine into a beaker and dilute with water. Add 1 or 2 cc. of dilute hydrochloric acid, and then titrate with the sulphite solution until the solution of iodine has become nearly colorless. Add starch and then more of the sulphite until the blue color has wholly disappeared. Titrate back to color with the standard solution

of iodine. The volume of the iodine solution employed to restore color must, of course, be added to the 10 cc. which were measured out in the first place. Calculate from the results the percentage of Na_2SO_3 in the sulphite.

Repeat the experiment, omitting the hydrochloric acid.

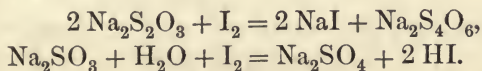
The order of the titration, i.e. the addition of the sulphite to the iodine, cannot be reversed except in the case of exceedingly dilute solutions, because in even moderately dilute solutions of sulphurous acid the hydriodic acid which is formed when iodine is introduced reacts upon a portion of the remaining sulphurous acid with formation of water and liberation of sulphur and iodine:



The iodine thus liberated reacts at once upon another portion of the sulphurous acid and water with formation of sulphuric acid and more hydriodic acid. Hence the reaction between sulphurous acid and iodine is regular, i.e. in accordance with the equation $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} + \text{I}_2 = \text{H}_2\text{SO}_4 + 2 \text{HI}$, only when the iodine is in excess.

The reaction $\text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{I}_2 = \text{Na}_2\text{SO}_4 + 2 \text{HI}$ is sometimes employed in standardizing acids. If the strength of the iodine solution is known, and the sulphite is neutral, the quantity of hydriodic acid which will be formed can be calculated. It may be employed to standardize a solution of iodine. For this purpose a solution of neutral sulphite of unknown strength, but dilute, is added to a measured portion of the iodine solution to be standardized until the color disappears. The hydriodic acid is then determined by means of some standard alkali. Methyl orange should be used as the indicator.

It will be seen from the following equations that it is practicable, with a standard solution of iodine, to determine a neutral sulphite and a thiosulphate when the two occur in the same solution:



The sum of the sulphite and thiosulphate is found from the iodine consumed in both reactions, while the sulphite is estimated separately by neutralizing the hydriodic acid with a standard alkali.

III. IODOMETRIC DETERMINATION OF CHROMIC ACID

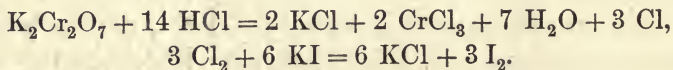
Weigh from 0.1 to 0.2 gram of pure potassium bichromate into a chlorine apparatus of the form represented in Fig. 45. Drop in a small piece of compact magnesite which is free from



FIG. 45

ferrous iron, and fill the flask half full of concentrated hydrochloric acid which contains no free chlorine. Pour about 50 cc. of potassium iodide solution of the usual concentration (1 : 10) into the receiver and connect the two parts of the apparatus as shown in the figure. Cautiously heat the flask until the reduction of the chromate is complete and all of the chlorine has been driven over into the receiver. With the lamp in one hand continue to heat the flask, and with the other hand withdraw the receiver until the curved end of the delivery tube is above the solution of potassium iodide. Immerse the closed end of the receiver in cold water and shake up the liquid from time to time to hasten the absorption of iodine vapors. Empty the receiver, introduce a fresh portion of iodide solution, connect up the apparatus, and heat again in order to ascertain whether all of the chlorine was distilled over in the first operation. Determine the iodine with the standard solution of thiosulphate.

The following equations represent the reactions which are involved in the determination:



Any other oxygen compound which liberates from hydrochloric acid a definite quantity of chlorine can be determined in

the same manner provided it is free from substances which, like iron in ferrous salts, absorb chlorine or convert it into chlorides.

IV. IODOMETRIC DETERMINATION OF ARSENIOS ACID

Weigh from 0.1 to 0.2 gram of pure resublimed arsenious oxide, and from 0.2 to 0.4 gram of pure potassium bichromate, into the chlorine evolution flask. Add concentrated hydrochloric acid and a piece of magnesite. Put the same quantity of potassium iodide solution into the receiver as before. Connect the two parts of the apparatus, and allow the mixture to stand for an hour or more before heating and then proceed as directed under III.

The difference between the quantity of iodine found and the quantity which the known weight of bichromate would have yielded in the absence of any reducing substance is due to the following reaction, by which the arsenious oxide has been converted into arsenic acid at the expense of a part of the chlorine :



There is therefore a deficit of four atoms, or 503.56 parts, of iodine for each molecule, or 196.54 parts, of the arsenious oxide.

EXERCISE XVIII

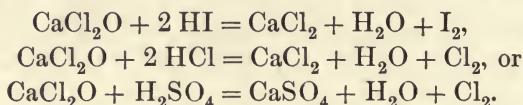
DETERMINATION OF HYPOCHLOROUS ACID

I. BY WAGNER'S METHOD

Weigh about 5 grams of bleaching powder — taking care to have the weighing glass tightly closed while in the balance case — into a porcelain mortar and grind the material fine with a little water. Add more water and transfer the liquid through a funnel to a half-liter measuring flask. Grind what remains in the mortar again with water, etc., until all the material has been brought into the flask. Fill to the mark with water. Shake up the contents of the flask, and, without giving the

suspended matter time to subside, measure 10 cc. of the liquid into a beaker with a pipette. Add about 100 cc. of water and 6 cc. of the usual solution of potassium iodide. Acidify with dilute hydrochloric acid, and determine the iodine with the standard solution of sodium thiosulphate.

The iodine liberated is equivalent to the active chlorine in the bleaching powder, i.e. the chlorine which would be liberated if the material were treated with any acid :



There are two ways of stating the quantity of active chlorine in bleaching powder. One gives the volume of the chlorine, under standard conditions of temperature and pressure, which a unit weight of the powder will yield, and the other the percentage of the same by weight.

A specimen which yields 100 cc. of chlorine per gram, or 100 liters per kilogram, of the material would be said to have 100 *chlorometric degrees*, or 100 degrees Gay-Lussac. A cubic centimeter of chlorine weighs 3.16742 milligrams at latitude 45° and sea level. A 100-degree bleaching powder must therefore contain 31.67 per cent of active chlorine. The results of the determination should be stated in both ways.

II. BY PENOT'S METHOD

There are required for this experiment :

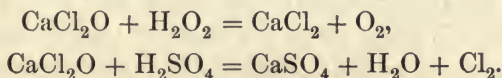
1. Starch-iodide papers for the detection of hypochlorous acid. Grind together in a porcelain mortar 1.5 grams of starch and 125 cc. of water. Boil the mixture for a few minutes. Add 0.5 gram of potassium iodide and an equal weight of crystallized sodium carbonate. Dilute with water to 250 cc. Saturate strips of white filter paper with the solution and dry them. Keep the papers in a closed vessel.

2. A standard solution of sodium arsenite. To prepare this, dissolve 2.211 grams of pure arsenious oxide in 300 to 350 cc. of hot water to which 6.5 grams of pure crystallized sodium carbonate have been added. Dilute the solution, when cold, to one half-liter. Each cubic centimeter of the solution is equivalent to one cubic centimeter of chlorine gas when measured under standard conditions of temperature and pressure, or to 3.16742 milligrams of the same.

3. A solution of the bleaching powder which is to be tested. This is prepared in the same manner as that which was used with Wagner's method. It is convenient, however, to employ a solution one cubic centimeter of which contains 0.010 gram of the original material. In all cases the solution should be well shaken just before measuring out the portion which is to be tested.

Measure into a beaker the quantity of the solution which contains 0.5 gram of bleaching powder. Titrate into it, slowly and with constant stirring, the standard solution of sodium arsenite until a drop of the liquid taken out with a glass rod and applied to the starch-iodide paper no longer gives a blue color. If exactly one half-gram of the material was employed for the determination, the number of cubic centimeters of the sodium arsenite used, multiplied by 2, is equal to the number of the degrees Gay-Lussac of the sample; and the number of cubic centimeters used, multiplied by 3.16742, gives the number of milligrams of active chlorine found.

Another method of determining the active chlorine in bleaching powder, which is rapid and fairly accurate, is that proposed by Lunge. It depends upon the fact that when a hypochlorite and hydrogen peroxide are brought together, a volume of oxygen is evolved which is exactly equal to that of the available chlorine in the hypochlorite:



The measurement of the liberated oxygen is therefore equivalent to a measurement of the chlorine which would be evolved if the material were treated with an acid as represented in the second equation.

The determination is made by placing a known weight of the bleaching powder — prepared with water, as previously directed — in a small flask and then lowering into the flask a flat-bottomed tube containing an excess of hydrogen peroxide. The flask is attached to a Hempel burette, or to some other suitable gas-measuring tube, which is partly filled with water. The height of the water in the burette is read, the tube containing the peroxide overturned, and the increase in the volume of the gas determined.

It will be seen that by reversing the process — i.e. by adding an excess of hypochlorite to a known volume of hydrogen peroxide — the strength of any solution of the peroxide may be determined by means of the same reaction. As a matter of fact, the method is rather more satisfactory for the determination of hydrogen peroxide than for the determination of a hypochlorite, because the evolution of oxygen in the latter case does not wholly cease with the destruction of the hypochlorite. The continued liberation of oxygen is due to a so-called catalytic decomposition of the excess of peroxide. It is, however, so slow that fair determinations of the hypochlorite may be made in spite of it.

EXERCISE XIX

DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS

I. BY THE LIME METHOD

In a narrow combustion tube, about 400 mm. in length and closed at one end, place a layer 60 mm. in length of pulverized lime which has been prepared from marble and is free from chlorine. Upon this place about 0.2 gram of pure chloral hydrate. Add another layer of lime of about the same length as the first.

Mix the materials with a wire, and then fill the tube nearly full of the lime. Hold the tube in a horizontal position and tap it upon the table until there is formed at the top a channel of sufficient size for the escape of gases. Place the tube in a combustion furnace and heat the lime near the open end to redness. Then, beginning at the heated end, light the other burners under the tube, one after another, and at considerable intervals of time. Having kept the whole tube at a red heat for twenty minutes or half an hour, cool it slowly and uniformly. Wipe the outside and transfer the contents to a beaker containing considerable water. Rinse the tube with water to which a little nitric acid has been added. Treat the contents of the beaker with dilute nitric acid (free from chlorine) until the liquid becomes permanently acid. It is not necessary to dissolve the whole of the solid material. The lime usually contains some silicate which is not readily decomposed by the acid. Filter through a small paper, and determine the chlorine in the filtrate, either gravimetrically or by the method of Volhard.

Instead of emptying and cleansing the tube in the manner prescribed, it may be closed with a stopper and placed, still hot, in a high beaker which is two-thirds full of cold water. In this way, it will be broken into small pieces, which, together with the carbon and other insoluble material, are filtered out after the treatment with dilute nitric acid.

If, as often happens, the lime, notwithstanding its preparation from marble, contains chlorine, the percentage of the latter must be determined and the lime employed in the experiment must be weighed. The chlorine belonging to the lime may then be deducted from the total found.

If compounds containing considerable nitrogen are decomposed by lime, there is a formation of cyanogen, and the precipitate obtained with silver nitrate is then a mixture of chloride and cyanide. The formation of cyanogen may be avoided by decomposing nitrogenous halogen compounds with soda-lime instead of lime.

Bromine and iodine are determined by the lime method in the same manner as chlorine. It is necessary, however, especially in the determination of iodine, to add a little sulphurous acid to the solution before precipitating with silver nitrate.

Liquid substances are weighed and introduced into the combustion tube in small bulbs blown on the ends of capillary tubes. The bulbs should be capable of holding about twice the quantity of liquid which is required for the analysis, and the tubes to which they are attached should be from 75 to 100 mm. in length. After weighing the bulb, the outlet is immersed in the liquid, which may then be made to rise into the bulb by alternately heating and cooling the bulb or by placing the vessel containing the liquid under the bell of an air pump and exhausting. The bulb is wiped dry, closed by holding the open end in the flame of a Bunsen burner, and weighed. Before introducing it into the combustion tube, the capillary tube is scratched with a file at a little distance from the base, and broken off. Both parts are then dropped into the lime or soda-lime in the bottom of the combustion tube.

II. BY CARIUS' METHOD

In a thick combustion tube — having a length of 400 or 500 mm. and an internal diameter of 13 to 15 mm., and closed at one end — place from 2.5 to 3 cc. of nitric acid of 1.5 specific gravity. In a narrow tube, 75 or 100 mm. long, weigh about 0.2 gram of chloral hydrate, and add to it about four times its weight of crystallized silver nitrate. Place the smaller tube in the larger one and draw out the open end of the latter to a capillary with thick walls, taking care not to let the nitric acid and the substance come together until the tube is sealed. The explosions which so often occur when substances are heated in closed tubes are usually due to a faulty sealing of the tubes. It is well, therefore, for one not experienced in this kind of manipulation to practice for a time — under supervision if possible —

with odd pieces of glass tubing before attempting to seal the tube which is to be used in this exercise. It is important that the wall of the drawn-out portion of the tube should be made quite thick at every point, and the glass should be well annealed by turning it in the smoky flame until it is densely and uniformly covered with carbon.

Put the closed tube in an iron one, letting the capillary end project a little beyond the mouth of the latter. Place the two tubes in the "bomb" furnace and put an empty wooden box before it to receive the material which will be ejected if an explosion occurs. Gradually raise the temperature of the furnace to 250° , and keep it there for two hours. When the glass tube has cooled to the temperature of the room, take the capillary end between the thumb and forefinger and draw the tube forward under a folded towel; and as soon as it is out of the iron tube roll it up in the towel. The opening of the tube, which requires great caution, is best accomplished in the following manner: A 300- or 400-cc. beaker, partly filled with water, is tilted forward and secured in this position by a block; a burner is placed directly in front of the beaker; finally, the capillary end of the tube is uncovered and cautiously heated until the glass softens, swells out, and opens for the escape of the compressed gases within. The issuing material should, of course, be directed into the beaker. Cut the tube near the middle, — taking care that no fragments of glass fall into either part, — wash the contents into a beaker, nearly neutralize the excess of nitric acid with sodium carbonate which is free from chlorine, and determine the silver chloride in the usual manner.

Bromine and iodine in organic compounds may also be determined by the method of Carius. The author of the method recommends in the case of iodine compounds that the mixture of silver iodide and nitrate be heated until it fuses to a yellow liquid which solidifies on cooling to an opaque yellow mass.

This must afterwards be heated in the diluted liquid from one to two hours in order to effect a separation of the iodide and nitrate.

The halogens may be removed from many organic compounds by treating their aqueous or alcoholic solutions with sodium amalgam.

The Separation of the Halogens

Any two of the halogens, when the third is absent, may be determined by an indirect method. Suppose, for example, that chlorine and bromine, in the form of a chloride and a bromide, are in solution and are to be determined indirectly. The best procedure is as follows: The amount of silver required for the precipitation of both is ascertained by the volumetric method of Mohr; the precipitate of AgCl and AgBr is then collected, washed, dried, and weighed. If, for any reason, the method of Volhard is to be preferred to that of Mohr, the solution is diluted to a known volume and divided, one measured portion being used for the volumetric, and the remainder for the gravimetric, determination.

The calculation is as follows:

Atomic and Molecular Weights

$$\text{Ag} = 107.11, \quad \text{AgCl} = 142.29,$$

$$\text{Cl} = 35.18, \quad \text{AgBr} = 186.46.$$

$$\text{Br} = 79.35,$$

Let x = weight of chlorine,

y = " " bromine,

a = " " silver required to precipitate Cl and Br,

b = " " AgCl + AgBr.

Then $x + y = b - a$, and

$$\frac{142.29}{35.18} x + \frac{186.46}{79.35} y = b, \quad 4.04462 x + 2.34984 y = b;$$

$$x = 1.38651 a - 0.79646 b, \text{ and}$$

$$y = 1.79646 b - 2.38651 a.$$

Several methods have been proposed for the separation of bromine from chlorine, all of which depend upon the fact that certain oxidizing agents under certain conditions are capable of liberating bromine from bromides but not chlorine from chlorides. The bromine, when liberated, is expelled from the solution, — with the aid usually of a current of steam or air, — and is collected either in a solution of some alkali to which has been added a quantity of hydrogen peroxide in order to prevent the formation of a hypobromite, or in a solution of potassium iodide. In the latter case the equivalent quantity of liberated iodine is determined volumetrically by means of sodium thiosulphate.

Some of the oxidizing agents which have been employed for the liberation of bromine in a mixture of bromides and chlorides are:

1. Lead peroxide and acetic acid (Vortmann *).
2. Potassium permanganate and acid potassium sulphate (Berglund †).
3. Potassium permanganate and aluminium sulphate (White ‡).
4. Potassium permanganate and acetic acid (Jannasch and Aschoff §).
5. Potassium bichromate and sulphuric acid (Dechan, || Friedheim and Meyer **).
6. Ammonium persulphate (Engel ††).
7. Potassium permanganate and ferrous sulphate (Weiss ††).
8. Iodic acid (Bugarszky §§).
9. Potassium permanganate in the presence of copper salts (Baubingy and Rivals |||).

* *Zeitsch. anal. Chem.*, **19**, 352; **22**, 565, 566; **24**, 196; **25**, 172.

† *Ibid.*, **24**, 184.

‡ *Chem. News*, **57**, 283; **58**, 229.

§ See references cited under Exercise XX.

|| *Jour. Chem. Soc.*, **49**, 682.

** *Zeitsch. anorg. Chem.*, **1**, 407.

†† *Zeitsch. anal. Chem.*, **34**, 616.

‡‡ *Ibid.*, **34**, 615.

§§ *Zeitsch. anorg. Chem.*, **10**, 387.

||| *Comptes Rendus*, **124**, 859; **125**, 527, 607.

Iodine may be separated from chlorine and bromine in a mixture of halogen salts in various ways:

1. It may be liberated by nitrous acid,* which does not decompose hydrochloric or hydrobromic acid, and then removed from the solution, either by extraction with carbon bisulphide, or by passing a current of steam through the liquid. If extracted by carbon bisulphide, it is best determined by a standard solution of sodium thiosulphate. If, on the other hand, the liberated iodine is removed by steam, it is best to conduct the vapors into an alkaline solution of hydrogen peroxide, and to determine it, either volumetrically or gravimetrically, as silver iodide.

2. The iodine may be liberated by arsenic acid (Gooch and Browning†) and removed by evaporation and the resulting equivalent quantity of arsenious acid determined volumetrically as recommended by the authors of the method; or it may be removed with the aid of steam, collected in a solution of potassium iodide, and determined by sodium thiosulphate as recommended by Friedheim and Meyer.‡

3. The iodine may be precipitated by thallium nitrate (Hübner, Spezia, and Frerichs §); or, if the quantity of bromine is small, by palladium nitrate.

In the absence of bromine, iodine may be separated from chlorine by precipitating with thallium sulphate in the presence of ammonium sulphate and alcohol (Jannasch and Aschoff ||).

* See Fresenius, *Quant. Analyse*, 1, 659; also Gooch and others, *Zeitsch. anal. Chem.*, 30, 58; 34, 603.

† *Zeitsch. anal. Chem.*, 30, 60; *Zeitsch. anorg. Chem.*, 4, 178.

‡ *Zeitsch. anorg. Chem.*, 1, 407.

§ Fresenius, *Quant. Analyse*, 1, 661.

|| *Zeitsch. anorg. Chem.*, 1, 248.

EXERCISE XX

THE SEPARATION OF CHLORINE, BROMINE, AND IODINE

BY THE METHOD OF JANNASCH AND ASCHOFF *

The apparatus which is recommended by the authors of the method is shown in Fig. 46.

It consists of:

1. A metallic vessel *a*, in which steam is produced for the expulsion of iodine and bromine.

2. The flask *b*, with a capacity of about one liter, in which the iodine and bromine are successively liberated — the former by nitrous acid and the latter by potassium permanganate and acetic acid.

3. The thin flask *c*, with a capacity of about 500 cc., which contains a solution of sodium hydroxide

and hydrogen peroxide, and is cooled by running water.

4. The Peligot tube *d*, which also contains a small quantity of the alkaline solution of hydrogen peroxide.

5. The Erlenmeyer flask *e*, containing a dilute solution of caustic soda to which a little ammonia has been added.

The required reagents are:

1. A 10 per cent solution of sodium nitrite.
2. A 5 per cent solution of sodium hydroxide.
3. A 3 per cent solution of hydrogen peroxide.
4. A 30 per cent solution of *pure* acetic acid.
5. A nearly saturated solution of potassium permanganate (approximately 5 per cent).

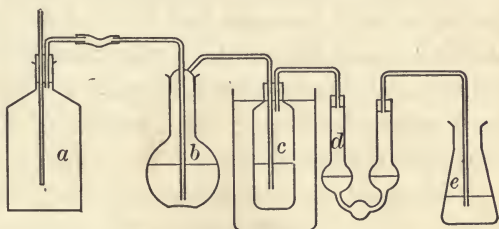


FIG. 46

* *Zeitsch. anorg. Chem.*, 1, 144; 5, 8.

All of the reagents must be free from halogens, and the acetic acid must be free from substances with which the halogens form substitution products.

Weigh out about one quarter gram each of pure chloride, bromide, and iodide of potassium. Introduce the salts into the flask *b*, dissolve in water, and dilute to about 750 cc.

Measure 100 cc. of a mixture of equal volumes of the sodium hydroxide and hydrogen peroxide solutions into the flask *c*, and a few cubic centimeters of the same mixture into the Peligot tube *d*. In the Erlenmeyer flask *e* place a small quantity of the caustic soda solution and add to it a little ammonia.

Having brought the water in *a* to the boiling point, add to the solution of the salts first 5 cc. of dilute sulphuric acid, and then 10 cc. of the solution of sodium nitrite. Close the flask quickly and conduct steam through it until all of the iodine has been removed, heating the contents of the flask in the meantime with a small flame.

Disconnect the absorption apparatus while the steam is still passing through, and transfer the contents of *c* and *d* quantitatively to a porcelain dish, keeping the liquid in *e* separate.

Make the solution of chloride and bromide in *b* distinctly alkaline with caustic soda and concentrate it in a porcelain dish to a volume of 50 cc. Return the solution to *b* and allow it to cool. Arrange and refill the absorption apparatus as for the collection of iodine, and introduce into *b* 60 cc. of the 30 per cent acetic acid and the volume of the permanganate solution which contains 1 gram of the salt. Heat the flask with a small flame and pass steam through it for not less than an hour after the contents have reached the boiling point.

Determination of the Iodine

Heat the liquid derived from *c* and *d* — which probably contains all of the iodine — for a long time in a covered porcelain

dish, add 50 cc. of the hydrogen peroxide solution to complete the oxidation of any sodium nitrite which may be present. Afterwards add the contents of the Erlenmeyer flask *e*, and concentrate to a suitable volume. To the alkaline solution add silver nitrate, little by little, and stir until the brown oxide of silver which is first formed is no longer converted into the yellow iodide. Acidify with nitric acid and heat for some hours upon the water bath, or until the precipitate has properly subsided. Filter hot, wash with boiling water, etc.

Determination of the Bromine

Heat the contents of *c* and *d* in a covered porcelain dish with an additional quantity of hydrogen peroxide in order to destroy any sodium hypobromite which may be present. Add the liquid in the Erlenmeyer flask and concentrate. Precipitate the bromine with a mixture of equal parts of 10 per cent silver nitrate solution and concentrated nitric acid. Heat from one to two hours on the water bath, filter hot, wash with boiling water, etc.

Determination of the Chlorine

Reduce the excess of permanganate with an ammoniacal solution of hydrogen peroxide. Collect the oxide of manganese upon a roomy filter and wash with a one per cent solution of sodium nitrate. Determine the chlorine in the filtrate as silver chloride.

If the liquid in which the three halogens are to be determined contains calcium, the use of sulphuric acid to decompose the nitrite for the purpose of liberating iodine is inadmissible. In such a case the authors of the method acidify the solution with a few drops of acetic acid and then conduct into the flask from the outside the vapors of nitrous acid until the space above the liquid begins to fill with the yellowish-red gas.

Jannasch and Koelitz* have found that when the halogens are to be determined in an alkaline liquid, either sulphuric or nitric acid — and *not acetic acid* — should be employed to neutralize the solution, since the presence of acetates — but not of sulphates or nitrates — retards the quantitative liberation of bromine.

To determine the halogens in organic compounds the authors† proceed as follows:

If the substance is to be decomposed by the “lime method,” a hard glass tube — about 50 centimeters long and having an internal diameter of 4 mm. — is filled to a depth of 3 or 4 centimeters with quicklime. The material — previously mixed with lime in a deep porcelain mortar — is then introduced. Afterwards the mortar, funnel, etc., are rinsed a number of times with small portions of finely ground lime, which are likewise filled into the tube until there remains room only for a plug of asbestos. After heating in the usual manner, the cooled contents of the tube are transferred to a glass-stoppered liter flask containing about 300 cc. of water. The tube is rinsed first with water and then with dilute nitric acid. Strong nitric acid, in small quantities, is then added until only a small portion of the lime remains undissolved, care being taken constantly to agitate the contents of the flask and to keep them cool. If, accidentally, the whole of the lime is dissolved, more must be added in order to produce an alkaline condition. After filtering and washing the solid residue with hot water, the halogens are precipitated with a mixture consisting of equal parts of concentrated nitric acid and a 10 per cent silver nitrate solution. The silver salts are heated upon a water bath, with frequent agitation, for an hour or more, or until the precipitate has fully subsided, and then collected upon a small paper filter. The washed contents of the filter — together with the still moist paper — are transferred to a silver crucible and fused with 5 or 6 grams of pure sodium hydroxide until the paper is fully burned and a

* *Zeitsch. anorg. Chem.*, 15, 66.

† *Ibid.*, 15, 68.

tranquil liquid is obtained. Finally, the residue is treated with water, warmed upon a water bath, filtered, the excess of alkali neutralized with sulphuric or nitric acid, and the halogens separated in the manner prescribed in Exercise XX.

The procedure with the silver salts is identical with that described above when the organic compound is decomposed by the method of Carius. They are collected upon a paper, washed, transferred — still wet — to a silver crucible, fused with sodium hydroxide, etc.

CHAPTER X

SULPHUR

EXERCISE XXI

THE DETERMINATION OF SULPHURIC ACID IN BARIUM SULPHATE

Weigh in a platinum crucible from 0.3 to 0.4 gram of pure, finely pulverized and dried heavy spar. Add about five times as much sodium-potassium carbonate which is free from sulphates, and fuse over the blast lamp until the decomposition is believed to be complete. Place the crucible on its side in a porcelain dish, cover it with distilled water, and heat until the excess of the carbonate and the alkali sulphates are dissolved. Filter, and wash the barium carbonate with water to which a little ammonia and ammonium carbonate have been added. Slightly acidify the filtrate with hydrochloric acid. Dilute, if necessary, to a volume of 100 or 150 cc.; heat nearly to the boiling point, and precipitate the sulphuric acid (slowly and with constant stirring) with a dilute hot solution of barium chloride, taking care to add a slight excess of the latter. Continue to heat the liquid for an hour, at least, and then put aside to settle.

When the liquid above the precipitate has become perfectly clear, pour it through a small filter. Treat the precipitate remaining in the beaker with boiling water containing a little hydrochloric acid, and pour this also through the paper when the barium sulphate has subsided. Wash the precipitate several times in this manner, and then bring it upon the filter. Wash again with hot water until the filtrate gives no reaction for chlorine.

Detach the edge of the filter from the glass with the aid of a stout platinum wire flattened at one end, or a thin spatula, and lift it out of the funnel. Examine the glass carefully for precipitate which may have crept over the edge of the paper, and, if any is found, wipe it up with a fragment of ashless paper which is afterwards to be placed in the filter. Fold the filter, without drying, into a compact wad, and place it in a weighed platinum crucible. The subsequent incineration requires some caution. The crucible, tilted to one side, is placed in a triangle which rests upon the ring of an iron stand. At first the ring is raised considerably above the flame, where it is kept until the paper is dry. Afterwards it is lowered from time to time until the charring process is finished, but never so far that the volatile products burst into flames. Finally, when nothing remains of the paper except carbon, the crucible is lowered into the flame and the incineration completed. The residue of carbon should burn quite readily, leaving a perfectly white ash. If it does not, measures should be taken to promote the circulation of air over the heated material. To this end the lamp is so placed that only the bottom of the tilted crucible is in contact with the flame; and the lid, with its edge resting on the triangle, is allowed to lean against the mouth of the crucible. It is quite practicable, of course, in cases of difficult incineration to introduce into the crucible a current of air or of oxygen through a small glass tube.

It is recommended by Richards, in precipitating sulphuric acid by barium chloride, to allow the solution of the latter to flow in a thin stream down the side of the beaker containing the former. The liquid spreads out in its passage over the glass wall, thus giving a great surface of first contact between the two solutions. The following manipulation of this method of precipitation has been found very satisfactory: By rotating the beaker in the hand, the hot solution of sulphate is given a somewhat rapid circular motion. The beaker is then placed on the sand bath or wire gauze, and the hot solution of chloride is

slowly poured down the side. When the movement of the liquid becomes too sluggish, the beaker is taken from the bath and again rotated. With proper management a precipitate is obtained which subsides completely within a few minutes.

When sulphuric acid is precipitated by barium chloride, some of the latter is always occluded by the barium sulphate, and no amount of washing suffices for its complete removal. The sulphate, however, is somewhat soluble, and under favorable conditions of precipitation the two sources of error nearly compensate each other. The occlusion is greater in concentrated than in dilute solutions. It is greater also in cold than in hot solutions. According to Richards the occlusion is increased by the presence of hydrochloric acid, but not by the addition of barium chloride after the precipitation of the sulphuric acid has been completed. The quantity of chloride which is carried down by the sulphate is greater when the latter is formed in the presence of an excess of the former, i.e. when the sulphuric acid or soluble sulphate is added to the solution of the barium salt; hence in precipitating, whether for the determination of sulphuric acid or of barium, the solution of the barium salt is poured into that of the sulphate. This order should never be reversed. The amount of the occluded chloride can be ascertained by fusing the precipitated sulphate with an alkaline carbonate and determining the chlorine as silver chloride.

The solubility of barium sulphate varies somewhat with the circumstances under which it is precipitated; it is given as one part in 400,000 parts of water under the usual conditions of precipitation. The precipitation is retarded even by very dilute hydrochloric acid, while in the presence of the moderately concentrated acid it is quite incomplete. The presence either of a soluble barium salt or of a sulphate (anything furnishing an ion in common with it) diminishes its solubility; hence the practice

in this case, as in quantitative work in general, of adding an excess of the precipitating agent. It is dissolved by concentrated sulphuric acid and reprecipitated on dilution with water. For further information regarding the solubility of barium sulphate see Fresenius and Hintz, *Zeitschrift für analytische Chemie*, **35**, 170.

There is some danger when the filter is burned too rapidly, i.e. at too high a temperature, that a little of the sulphate will be reduced to sulphide, which may be converted by the water vapor and carbon dioxide surrounding it first into hydroxide and afterwards into carbonate. It is therefore well to moisten the material, after the first ignition and weighing, with a drop of sulphuric acid, and then to evaporate, ignite, and weigh again.

EXERCISE XXII

DETERMINATION OF SULPHUR IN SULPHIDES

The nitric acid which is to be used in this and in a subsequent experiment is to be prepared in the following manner: Pour into a tubulated liter-and-a-half retort, first 200 cc. of concentrated nitric acid, and then 600 cc. of concentrated sulphuric acid. Fasten the retort in a clamp, and — without boiling the mixture — slowly distill about 100 cc. of the nitric acid into a receiver which fits the retort closely. The distillate will probably contain sulphuric acid, which must be removed. Place one or two grams of pulverized and thoroughly dried barium nitrate in a glass-stoppered bottle and add the nitric acid to it. Shake the bottle from time to time for several hours. Pour the acid into a small retort and distill it slowly into a receiver. The distillate must now be tested for sulphuric acid. Place about 5 cc. of it in a clean dry retort, add about half a gram of pure potassium nitrate, and distill to dryness. Dissolve the residue in the retort in water, add a drop or two of hydrochloric acid, and test for sulphuric acid with barium chloride.

Solutions which are to be tested for sulphuric acid, or in which the presence of small quantities of that acid would be harmful, must not be evaporated in open vessels over the ordinary water bath. Owing to the presence of sulphur in the gas, solutions so treated almost invariably become contaminated with sulphuric acid.

Weigh into narrow, flat-bottomed tubes two portions (0.2 to 0.3 gram each) of finely ground pyrites. This mineral is selected because it contains iron, which introduces a certain difficulty into the determination of sulphuric acid as sulphate of barium. Pour into pressure bottles — so-called “Lintner bottles” — from 5 to 10 cc. of the nitric acid which has been prepared as directed. Set the tubes containing the weighed material in the bottles in an upright position. Fasten the latter in their frames, and then tilt them so that the tubes fall on their sides. Shake the bottles gently until the acid and the mineral are well mixed. When the reaction ceases, or becomes very slow, place the bottles in a bath containing cold water. Heat the water and keep it near the boiling point for two hours or more. Examine the contents of the bottles for undecomposed mineral and unoxidized sulphur. The presence of solid matter, when sulphides are treated in this manner, is not a certain evidence that the reaction is unfinished, since it may consist of sulphates which, though soluble in water, are insoluble or only slightly soluble in nitric acid. If the reaction is incomplete, heat again in the water bath as before. If, on the other hand, it appears to be complete, transfer the contents of the bottles to porcelain dishes. If the mineral contained no insoluble foreign matter, and the oxidation is finished, the diluted solutions will be clear. If they are free from suspended matter, add to each about 0.3 gram of pure potassium chloride to insure the presence of enough base to convert all of the sulphuric acid into sulphates, and evaporate to dryness at a low temperature on a broad sand bath. Treat the residues with strong hydrochloric acid and again evaporate to dryness. Repeat the addition of hydrochloric acid

and the subsequent evaporation until all the nitric acid has been removed. Treat the residues with a few drops of hydrochloric acid and dissolve them in water. If the solutions contain suspended matter, they are to be filtered.

Some sulphides, when decomposed with nitric acid in the manner just described, yield a deposit of free sulphur which is only very slowly converted into sulphuric acid. In such cases the bottles should be opened when cold and the contents treated with a little potassium chlorate or strong hydrochloric acid; after which they are to be closed and again gently heated. If this procedure fails to complete the oxidation of the sulphur, the diluted liquid must be filtered through a weighed paper, and the filter and its contents thoroughly washed, dried at constant temperature, and weighed. The residue on the paper, whose weight is determined in this manner, will consist of the unoxidized sulphur and any impurity in the mineral which has not been attacked by the nitric acid. The paper and its contents are therefore incinerated and the ash weighed. The loss during incineration is the weight of the unoxidized sulphur.

When sulphuric acid is precipitated by barium chloride in the presence of ferric salts, the barium sulphate carries down with it a quantity of iron, either as ferric sulphate or as a double sulphate of barium and iron, and the iron cannot be wholly removed even by washing the precipitate with dilute acids; neither can the precipitation of the iron be prevented by the presence of any quantity of acid which would not interfere with the completeness of the precipitation of the sulphuric acid. Again, when barium sulphate which is contaminated with ferric sulphate is ignited, the sulphuric acid in combination with the iron is volatilized, and the barium salt becomes colored from pink to brown by ferric oxide. But the weight of the oxide is not equal to that of the barium sulphate which the lost acid should have formed. It is therefore found that the results are

usually too low when sulphuric acid is determined in the ordinary manner in the presence of ferric salts. Various methods of obviating this difficulty have been proposed:

(a) Lunge * precipitates the iron as ferric hydroxide by adding a not too large excess of ammonia to the moderately warm solution, filters after 10 minutes, washes the precipitate with boiling water, and determines the sulphuric acid in the filtrate in the usual manner, i.e. by precipitating as barium sulphate in the presence of hydrochloric acid. If the ferric hydroxide is suspected of retaining sulphuric acid, it may be fused with sodium carbonate in a platinum crucible, the sodium salts dissolved in water, filtered, the filtrate acidified with hydrochloric acid, and tested with barium chloride.

(b) Fresenius † fuses the pulverized mineral in which sulphur is to be determined in a platinum crucible with ten parts of a mixture consisting of two parts of dry sodium carbonate and one part of potassium nitrate, extracts the soluble matter with warm water, conducts carbon dioxide into the filtrate to precipitate any lead which may be present, filters, boils the insoluble residue in a solution of sodium carbonate, filters again, and boils the residual solid matter with water to which a little sodium carbonate has been added. The filtrates and wash water are mixed, acidified with hydrochloric acid, warmed to expel carbon dioxide, and repeatedly evaporated in a porcelain dish with hydrochloric acid in order to expel the nitric acid and to render insoluble any silica which may be present. The residue is moistened with 2 cc. of hydrochloric acid, dissolved in water, filtered if necessary, and the sulphuric acid precipitated by barium chloride. The barium sulphate obtained in this way is frequently not quite pure; it is therefore heated repeatedly in the platinum crucible in which it was weighed with small portions of weak hydrochloric acid, which are poured, after dilution, through a small filter. The filtrate is treated with a little barium chloride and evaporated nearly to dryness on the water bath. The residue is treated

* *Zeitsch. anal. Chem.*, **19**, 419.

† *Ibid.*, **16**, 335.

with water and filtered through the small paper, which is afterwards burned, the ash being added to the main body of the barium sulphate. The purified material is usually found to weigh a little less than the original precipitate.

(c) C. Meineke* and O. N. Heidenreich† reduce the ferric salt to the ferrous condition with metallic zinc, filter, wash the undissolved metal, and precipitate the sulphuric acid in the filtrate with barium chloride.

(d) F. W. Küster and A. Thiel‡ treat the cold solution with an excess of dilute ammonia, heat nearly to the boiling point, add barium chloride, and then dissolve the precipitated ferric hydroxide with hydrochloric acid.

The solutions of the sulphide are to be treated by methods c and d.

1. *Method c*

Dilute one of the solutions in an Erlenmeyer flask to a volume of 200 or 250 cc., add granulated zinc — or filings of the metal — and hydrochloric acid; place a funnel in the mouth of the flask and warm upon a sand or asbestos bath until the reduction is complete. Filter hot — through a paper wet with boiling water — into a beaker, wash the undissolved metal and the filter, and precipitate the sulphuric acid with the usual precautions.

2. *Method d*

Dilute the remaining solution of the mineral to 70 or 80 cc. and precipitate the iron with a moderate excess of dilute ammonia. Heat nearly to the boiling point, stirring meantime, and then — without separation of the ferric hydroxide by filtration

* *Zeitsch. anal. Chem.*, **38**, 209, 351.

† *Zeitsch. anorg. Chem.*, **20**, 233.

‡ *Ibid.*, **19**, 97.

—precipitate the sulphuric acid with barium chloride. Dissolve the ferric hydroxide with dilute hydrochloric acid, and keep the liquid hot for two hours. After cooling to the temperature of the room, pour the liquid through a filter and digest the remaining barium sulphate for half an hour with water containing a little hydrochloric acid. Decant through the filter; repeat the digestion; wash several times with boiling water, by decantation; and then bring the precipitate upon the filter.

EXERCISE XXIII

THE DETERMINATION OF SULPHUR IN IRON BY FRESENIUS' METHOD

There are required for this experiment:

1. A Kipp's apparatus for the generation of hydrogen.
2. Three cylinders, or wash bottles, for the liquids employed to purify the hydrogen. The first, i.e. that next to the generator, is to contain a solution of caustic soda; the second, a neutral or slightly alkaline solution (under no circumstances an acid one) of potassium permanganate; and the third, a solution of lead hydroxide in caustic soda. The last is made by adding an excess of sodium hydroxide to a solution of lead nitrate.
3. A quarter-liter flask to contain the hydrochloric acid which is used to dissolve the iron. This is supplied with a doubly perforated rubber stopper, through which pass two glass tubes, both bent to a right angle. One of the tubes reaches to the bottom of the flask, and is covered with vaseline where it passes through the stopper in order that it may be easily raised and lowered. The other—the one which is connected with the washing apparatus—reaches only about halfway to the bottom of the flask. The flask is to be filled about half full of pure concentrated hydrochloric acid.
4. A 300- or 400-cc. flask in which to dissolve the iron. This, like the flask 3, is supplied with a doubly perforated

stopper and two glass tubes. One of the latter is long — reaching to the bottom of the flask — and is bent to a right angle. This is connected with the long tube in 3 by a piece of rubber tubing 100 or 150 mm. in length. This rubber tube, also that by which 3 is connected with 2, is provided with a Mohr pinch-cock. The second glass tube, which should be as wide as practicable, is bent to less than a right angle and is cut off even with the lower end of the stopper. The flask is to be placed on a tripod.

5. A short condenser with a comparatively wide inner tube. The condenser is fixed in an inclined position with its lower end attached to the tube in 4, which is bent to less than a right angle.

6. Two Peligot tubes, which are to be connected with each other and with the condenser. In these, corks, and not rubber stoppers, must be used. Both tubes are to be partly filled with strong hydrochloric acid in which from 3 to 5 cc. of bromine have been dissolved. At the exit end they are to be connected with a flask containing sodium hydroxide to which hydrogen peroxide has been added.

Weigh about 10 grams of cast-iron borings into the flask 4, and add a few cubic centimeters of water. Conduct hydrogen through the apparatus — with the Peligot tubes detached — until the air in it has been displaced. Attach the Peligot tubes, press down the long tube in 3, and let the hydrogen force a little hydrochloric acid into 4. Clamp the rubber tube between 3 and 4, and gently heat the flask 4. When the reaction becomes too moderate, introduce more acid in the same manner as before. When the solution of the iron has been completed, raise the long tube in 3, and again pass hydrogen through the apparatus. Transfer the contents of the Peligot tubes to a porcelain dish, add about a gram of pure potassium chloride, and evaporate to dryness at a moderate temperature. Dissolve the residue in water, add a little hydrochloric acid, and precipitate the sulphuric acid in the usual manner.

The insoluble matter in the flask — largely carbon — will probably contain a small amount of sulphur, and this must also be converted into sulphuric acid and determined with that already precipitated. Filter the contents of the flask and wash thoroughly, first with a little dilute hydrochloric acid and then with hot water. Dry the filter and brush the material in it into

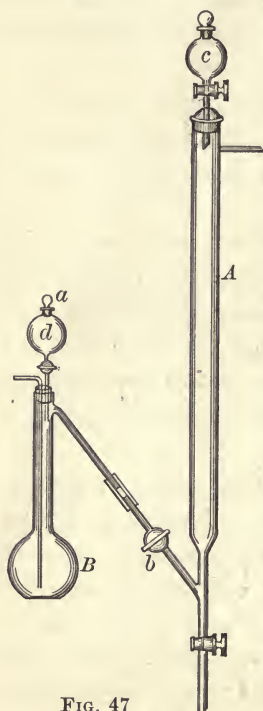


FIG. 47

a mortar. The small quantity of material which cannot be separated from the paper may safely be neglected. Add 10 grams of dry sodium carbonate and 5 grams of potassium nitrate, and grind to a uniform mixture. Transfer the contents of the mortar to a large platinum crucible and heat — raising the temperature quite gradually and only to the fusing point of the salts. Dissolve the cooled mass in water, filter if necessary, and evaporate the solution in porcelain to dryness with hydrochloric acid. Moisten the residue with strong hydrochloric acid and again evaporate to dryness, repeating the treatment until all the nitric acid has been expelled. Dissolve the residue in water, adding a few drops of hydrochloric acid, filter, and precipitate the sulphuric acid with barium chloride. Collect both portions of barium sulphate on the same filter.

All the materials used in the experiment must be examined for sulphur; and, if reagents free from it are not obtainable, the sulphur in them must be determined. It will then be practicable by working with weighed or measured quantities of the impure reagents to correct properly the final results.

This method for the determination of sulphur in iron can be applied with advantage to all those sulphides which are

decomposed by hydrochloric acid with a quantitative conversion of the sulphur into hydrogen sulphide.

A more convenient form of apparatus is shown in Fig. 47. The tube *A* is filled with beads or broken glass, and the bulb *c*, with the solution of bromine in hydrochloric acid. The iron, or the sulphide in which the sulphur is to be determined, is placed in *B*. The air in *B* is expelled by hydrogen which is purified in the manner already described, the gas being allowed to escape first at *a* and afterwards through *b*. The bulb *d* is then filled with hydrochloric acid which is admitted to the material below as occasion may require. Previous to the introduction of the acid, however, the broken glass in *A* is thoroughly moistened with the bromine solution in *c*. Afterwards the solution is allowed to flow from *c* as rapidly as may be necessary in order to keep the glass well colored by the bromine. The solution containing the sulphuric acid, which collects at the bottom of the apparatus, is



FIG. 48

drawn off from time to time into a beaker or flask; and when the operation is complete, the broken glass and the connecting tube *b* are rinsed with water into the same receptacle.

Still another very effective form of apparatus for the absorption of hydrogen sulphide and other gases is shown in Fig. 48.

Various other substances besides a solution of bromine in hydrochloric acid are employed to absorb or to oxidize hydrogen sulphide; for example, solutions of lead oxide in caustic alkali; of cadmium oxide in ammonia; of silver oxide in ammonia; of ammoniacal hydrogen peroxide; and of potassium permanganate. It may also be determined iodometrically:



EXERCISE XXIV

THE DETERMINATION OF SULPHUR IN ORGANIC
COMPOUNDS

I. BY LIEBIG'S METHOD

Place in a silver crucible about 10 grams of potassium hydroxide which is free from sulphur. Fuse (over an alcohol lamp if practicable), and continue to heat until the liquid becomes tranquil. Add from 1 to 1.5 grams of potassium nitrate and stir it into the molten hydroxide with a silver spatula. Allow the crucible to cool, and place on the top of the solidified mixture a weighed quantity of any non-volatile organic sulphur compound which contains about 20 milligrams of sulphur. Fuse the contents of the crucible, and continue to heat until the carbon which separates is all oxidized and the liquid becomes transparent. Dissolve in water, and evaporate the solution in a porcelain dish repeatedly with an excess of hydrochloric acid until all the nitric acid has been expelled. Dissolve the residue in water containing a little hydrochloric acid. Dilute to about a liter and allow the solution to stand for several hours, observing whether any silver chloride separates. If it becomes cloudy, filter. Evaporate in a porcelain or platinum dish to 150 or 200 cc. and precipitate the sulphuric acid in the usual manner with barium chloride.

If gas must be used, since it always contains sulphur, care must be taken to protect the contents of the crucible from the products of combustion, and the fusion should not be unnecessarily prolonged. It is to be remembered in this connection that much of the sulphur ordinarily in illuminating gas may be removed by passing the gas over a solution of lead oxide in sodium hydroxide.

II. BY CARIUS' METHOD

In a thick-walled tube of moderately soft glass — closed at one end and having a length of 450 or 500 mm. and an internal diameter of 15 to 18 mm. — place a weighed quantity of any pure organic sulphur compound which contains from 15 to 20 milligrams of sulphur. Calculate how much of the nitric acid which was prepared for use in Exercise XXII will be required for the complete oxidation of the compound, and measure about three times that amount into a narrow glass tube. Place the tube containing the acid in the larger one, taking care not to allow the acid and the substance to be oxidized to come in contact. Close the outer tube with great care as directed in Exercise XIX, II. Heat the tube also as there directed.

The temperature to which the bath must be raised and the length of time which it will be necessary to heat the contents of the tube will depend on the nature of the substance. If it is easily oxidized, two hours' heating at 200° will suffice. If it is attacked with difficulty by oxidizing agents — like some of the sulphur derivatives of the aromatic hydrocarbons, especially the sulphonic acids — it will be necessary to heat four or six hours at 250° or 260° .

Remove the tube from the bath and open it with all the precautions mentioned in Exercise XIX, II. Transfer the liquid containing the sulphuric acid to a porcelain dish, and add about a gram of pure potassium chloride. Evaporate with hydrochloric acid repeatedly to remove nitric acid, and determine the sulphuric acid as barium sulphate.

The ratio of the weight of the nitric acid, in grams, to the capacity of the tube in cubic centimeters should not exceed that of 1 to 12. In the case of substances requiring a high temperature for their decomposition, e.g. 300° , the tube may be heated for a time at a lower temperature, e.g. 250° , then cooled and opened to relieve the pressure. It may then be resealed and heated with safety to the required temperature.

Liquid substances which are too volatile for manipulation in open tubes are weighed in bulbs blown on the end of thin, nearly capillary tubes. A file mark made near the bulb will enable one to break off the stem after sealing the outer tube.

III. BY SAUER'S METHOD

For Liquids

The apparatus required for the experiment is shown in Fig. 49. A combustion tube 850 mm. long is narrowed down at the point *a* to a diameter of about 5 mm. The rear end is closed with a stopper through which passes one limb of the branching tube *b*, *c*. The front end is closed with a stopper through which

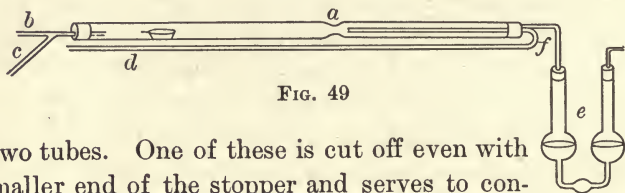


FIG. 49

pass two tubes. One of these is cut off even with the smaller end of the stopper and serves to connect the combustion tube with the Peligot tube *e*. The other, *d*, extends into the larger tube to the constriction *a*. The bend at *f* is made large so that the portion from *d* to *f* may lie outside of the furnace. If desired, the tube may be cut near *f* and the two parts joined by a piece of rubber tubing. The absorption apparatus *e* contains a solution of bromine in hydrochloric acid, and is connected in turn with another apparatus of the same kind which is partly filled with caustic soda to which hydrogen peroxide has been added. The tubes *c* and *d* are connected with a gasometer containing oxygen. The branch *b* is connected with a Kipp's carbon dioxide generator. Both gases are dried by calcium chloride before entering the combustion tube. The rubber connections of the tubes *b*, *c*, and *d* are provided with screw pinchcocks in order that the flow of the gases may be regulated.

In a bulb blown on the end of a narrow, thin tube, weigh a quantity of any pure liquid organic sulphur compound which contains from 15 to 20 milligrams of sulphur. Make a file mark near the bulb, and lay the bulb in a porcelain boat with the scratch underneath and the stem extending over the end of the boat. Place the boat in the combustion tube in the position indicated in the figure. Pass carbon dioxide through the apparatus and heat the combustion tube at *a* to redness. Remove the rear stopper, and break the tube containing the liquid by pressing upon it with a glass or iron rod just over the file mark. Replace the stopper quickly, slow down the current of carbon dioxide, admit oxygen through *d*, and cautiously warm the material. The flow of carbon dioxide through *b*, and of oxygen through *d*, also the heating of the substance, must all be so regulated that the combustion — which will consist of a series of flashes — will take place in the immediate vicinity of the constriction *a*. If the flame recedes towards the boat, the flow of carbon dioxide must be increased or the temperature must be increased. If it moves too far in the other direction, the flow of oxygen through *d* must be increased or the temperature of the substance lowered. When there is no more volatile matter to burn, cut off the carbon dioxide, admit oxygen through *c*, and heat the tube in the vicinity of the boat to redness. Fill the apparatus with carbon dioxide. Transfer the contents of *e* to a porcelain dish and rinse into the same all parts of the various tubes which have been in contact with the products of the combustion. Add potassium chloride, evaporate, and determine the sulphuric acid as barium sulphate.

Instead of a solution of bromine in hydrochloric acid, one may employ, as proposed by Burton, a standard solution of sodium carbonate to absorb the sulphur dioxide and neutralize the sulphuric acid, and determine the excess of the alkali volumetrically with use of methyl orange as the indicator.

When the method of Sauer is employed on substances which, like coke, yield no volatile products at high temperatures, the tube *d* is omitted and the material is burned in oxygen which enters the combustion tube at the rear end. No current of carbon dioxide is then required, and the tube need not be constricted at any point.

If a substance yields an ash, a portion of the sulphur may remain in the boat as an insoluble sulphate. The ash must then be fused with an alkaline carbonate, the mass treated with water, the solution filtered and evaporated to dryness with an excess of hydrochloric acid to render silica insoluble, and the residue digested with water containing a little hydrochloric acid. In the filtrate, the sulphuric acid is precipitated with barium chloride.

CHAPTER XI

NITROGEN

EXERCISE XXV

THE DETERMINATION OF NITRIC ACID

I. BY THE TIEMANN-SCHULZE METHOD

An apparatus like that represented in Fig. 50 is required. The flask should have a capacity of 150 or 200 cc. The rubber stopper must be a soft one and fit the flask tightly. The glass tubes which pass through it should also fit very closely. The right-hand tube, through which the nitric oxide escapes to the eudiometer, is cut off flush with the lower end of the stopper; while the left-hand tube, which serves for the introduction of ferrous chloride and hydrochloric acid, extends halfway down the neck of the flask and is drawn out to a fine point. Both of the tubes are cut and the parts rejoined by means of thick-walled but very flexible rubber tubing of the black variety. The connectors should be tied with waxed shoemaker's thread, and each is to be provided with a Mohr's pinchcock. The end of the exit tube, where it passes under the graduated tube, should be covered with rubber.

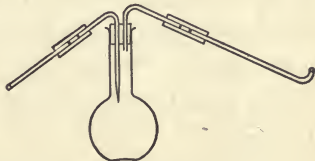


FIG. 50

Test the apparatus in the following manner: Fill the flask half full of water. Immerse the outlet of the right-hand tube in half a liter, and that of the left-hand tube in a few cubic centimeters of water. Boil the water in the flask down to a volume

of about 50 cc. Close the left-hand tube for a few minutes, then open it and close the right-hand tube for a time. Close the left-hand tube and remove the lamp. After 15 or 20 minutes, open the right-hand tube and allow the water to enter the flask. If it fills the flask completely, the apparatus is sufficiently tight.

Place about 40 grams of iron wire in a flask and pour over it 100 cc. of concentrated hydrochloric acid. When the reaction is nearly over, close the flask loosely with a cork.

Put half a liter of a ten per cent solution of caustic soda in a porcelain dish and boil the air out of it.

Weigh about one-tenth of a gram of pure potassium nitrate into the flask represented in the figure; and add to it water until the flask is half full. Insert the stopper and boil until the volume of the solution has been reduced to 40 or 50 cc. Close the left-hand tube and immerse the outlet of the right-hand tube in the solution of sodium hydroxide. After the steam has been conducted for a time into the caustic soda, close the right-hand tube and open the other with its exit end under water. When the volume of the solution in the flask has been reduced to about 10 cc., close the left-hand tube and remove the lamp.

Fill the eudiometer with the caustic soda, place a small paper filter on the convex end of the liquid column, and invert the tube with its open end in the solution of alkali. Tilt the eudiometer to one side to allow the paper, also the bubble of air which will probably be under it, to rise to the top, and then fix it in its position over the outlet of the exit tube. Introduce into the flask, through the left-hand tube, as soon as the diminished pressure will permit it, 20 cc. of the saturated solution of ferrous chloride, and afterwards about an equal volume of concentrated hydrochloric acid. In order to insure the removal of all the ferrous chloride from the tube, the acid is divided into two portions and introduced from separate vessels. It is convenient to take the chloride and the two portions of acid from

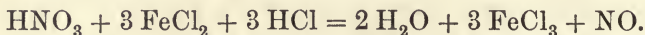
test tubes on which strips of paper have been pasted to indicate the quantities to be introduced. The lower of the two strips on each of the three tubes must, of course, be placed some distance above the bottom in order to avoid the danger of exposing the end of the tube through which the liquids enter the flask.

Warm the flask slowly, opening the pinchcock on the right-hand tube from time to time just far enough to ascertain which way the liquid in the tube will flow. As soon as the pressure within the flask is sufficient to force the nitric oxide into the eudiometer, remove the pinchcock and continue to heat until the volume of the gas no longer increases.

Place a small cup, having a handle, under the open end of the gas tube, and transfer it to a long glass cylinder which is nearly full of water. The cylinder should be nearly high enough to permit the complete submersion of the tube. After fifteen or twenty minutes, raise the tube with a pair of tongs until the water within and without is on the same level and read the volume of the gas. Submerge the tube for a short time, then raise it and read again. The second reading can be made more quickly than the first, and is necessary because of the effect of the evaporation from the wet glass upon the volume of the gas. Note the temperature of the water in the cylinder and the height of the barometer. Correct the volume of the gas to standard conditions of temperature and pressure and also for the water vapor which it contains. One cubic centimeter of nitric oxide weighs under standard conditions 1.34192 milligrams.

This method is sufficiently accurate for ordinary purposes. There are, however, several sources of error in it: The hydrochloric acid contains air; the nitric oxide is somewhat soluble in caustic soda, and more soluble in water; and, finally, the free oxygen in the water unites with some of the nitric oxide, converting it into NO_2 , and this is decomposed by the water with the formation of nitrous and nitric acids.

The reaction which takes place when nitric acid, ferrous chloride, and hydrochloric acid are brought together may be represented by the following equation:

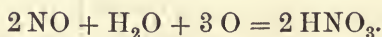


It is not influenced by the presence of organic matter, and for that reason is usually employed for the determination of nitric and nitrous acids in water analysis.

There are various methods, besides the measurement of its volume, by which the nitric oxide may be determined:

1. Pelouze, who was the first to employ the reduction of nitric acid by ferrous chloride for quantitative purposes, added to the acid a known quantity of the ferrous salt and titrated the excess with potassium permanganate. But owing to the reconversion of the nitric oxide into nitric and nitrous acids by the oxygen of the air and the water vapor within the flask, to the difficulty of wholly expelling the nitric oxide, and to the loss of nitric acid by evaporation, the method in its original form has been abandoned. It has, however, been so modified by Fresenius (*Quantitative Analyse*, 1, 520) as to give excellent results. The modification consists in the expulsion of the air and the nitric oxide from the vessel in which the nitric acid is reduced by a current of hydrogen or of carbon dioxide, and in the titration of the excess of the ferrous chloride by potassium bichromate or of the ferric chloride by stannous chloride.

2. Another excellent method is that proposed by Schloesing, and variously modified in its details by others, according to which the nitric oxide is converted into nitric acid and the latter determined by means of a standard solution of alkali. The reaction may be represented as follows:



3. The nitric oxide may also be estimated by determining its reducing action on a standard solution of potassium permanganate.

II. BY CRUM'S METHOD

Turn the three-way stopcock of the Lunge nitrometer, represented in Fig. 51, so that the graduated portion of the tube is in communication with the funnel above. Raise the reservoir tube and pour mercury into it until the metal runs into the funnel. Turn the stopcock so as to allow the mercury in the funnel to flow out at the side and then turn it again so as to close the funnel. Place in the bottom of the funnel about 100 milligrams of pure potassium nitrate. Dissolve it in the least possible quantity of water, using a platinum wire as a stirring rod. Lower the reservoir tube so as to produce a slightly diminished pressure. Open the stopcock cautiously and let the solution of nitrate run slowly into the tube below, closing it again before the air enters the stopcock. Pour about 1 cc. of pure concentrated sulphuric acid into the funnel, and with the platinum wire rub it over the glass wherever it is wet with the aqueous solution of the nitrate. Let the sulphuric acid into the tube below and repeat the washing of the funnel with 1-cc. portions of sulphuric acid until from 6 to 8 cc. have been introduced into the graduated tube.

Shake the tube vigorously up and down for five minutes, taking care, however, not to allow the acid to come in contact with the rubber tube.

When the apparatus has cooled to the temperature of the room, agitate again in order to ascertain whether the reaction is finished. Raise or lower the reservoir until the mercury in it stands above that in the measuring tube by a distance equal to one-seventh the length of the sulphuric acid column, and read the volume of the gas. Note the temperature and the height of the barometer. To determine whether the pressure under which the gas was measured is really equal to that of the air,

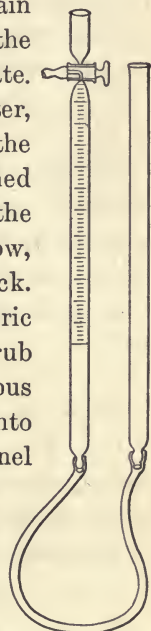


FIG. 51

open the stopcock and observe whether the mercury in the graduated tube rises or falls and to what extent. If any change in the level of the mercury takes place, twice the amount of that change, measured in millimeters, must be added to or subtracted from the height of the barometer when the volume of the gas is reduced to standard pressure. If the mercury rises on opening the stopcock, the correction is to be added; if the mercury falls, it is to be subtracted.

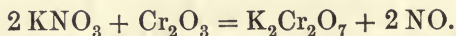
The reduction of nitric acid by mercury and sulphuric acid may be represented as follows:



Nitrous acid and nitrogen dioxide are also reduced to nitric oxide by mercury and sulphuric acid. The reaction is not affected by the presence of organic matter, and it may therefore be employed in water analysis. The method is especially adapted to the determination of oxides of nitrogen in sulphuric acid.

There are various other methods of determining nitric acid.

One of them, Wagner's, like those already given, involves the reduction of the acid to nitric oxide. It is based on the reaction which takes place when a nitrate is heated with chromium oxide in the presence of an alkaline carbonate:



Either or both of the products of the reaction may be determined.

Another method which is sometimes employed in water analysis is founded on the fact that nitric acid destroys the color of indigo solution.

There are also several methods based on the reduction of nitric acid to ammonia. This can be effected in a variety of ways, but most readily by the action of a metal or a pair of metals on an alkaline solution of a nitrate. The metals usually employed are aluminium, platinum and zinc, iron and zinc, zinc and copper.

EXERCISE XXVI

COLORIMETRIC DETERMINATION OF NITROUS ACID BY
THE METHOD OF GRIESS, PREUSSE, AND TIEMANN

The reagents required for this experiment are:

1. A dilute solution of metadiamidobenzene, which is made by dissolving 1.25 grams of the base, or an equivalent amount of a salt, in water, slightly acidifying with dilute sulphuric acid, and diluting with water to 250 cc. If the solution is colored, it must be filtered through charcoal or agitated with a small amount of the same and then filtered.

2. Dilute sulphuric acid prepared by dissolving one volume of the strong acid, free from nitrous acid, in two volumes of water.

3. A standard solution of potassium nitrite containing in each cubic centimeter 0.01 milligram of N_2O_3 . This is obtained by dissolving 0.4047 gram of pure and dry silver nitrite in hot water and adding to the solution an excess of potassium chloride. After cooling, the solution is diluted to a liter, and, when the silver chloride has subsided, 100 cc. of it are withdrawn and again diluted to a liter.

The silver nitrite is prepared by mixing a warm concentrated solution of 10 parts of potassium nitrite with a warm concentrated solution of 16 parts of silver nitrate. The precipitate, when cold, is washed on a filter with cold water, and dried, first by drawing air with the aid of the filter pump through the funnel (tightly covered with a filter paper), and then in a desiccator protected from the light. Or it may be quickly dried over a water bath. In the latter case, however, it is apt to suffer a slight decomposition.

There are also required four uniform graduated glass cylinders such as are employed in the colorimetric determination of ammonia and known under the name of Nessler tubes, and two burettes, one for the sulphuric acid and the other for the metadiamidobenzene.

For the experiment a specimen of well water containing nitrous acid, or a portion of the standard solution of nitrite diluted to a known degree by another person than the experimenter may be used.

Place a measured portion of the solution to be tested in one of the cylinders, add 1 cc. of the sulphuric acid and 1 cc. of the metadiamidobenzene solution, fill to the mark on the cylinder with water, stir with a glass rod, and watch the color which is developed. If it contains even the slightest shade of red, the solution is too concentrated and measured portions of it must be diluted with measured quantities of water until only light shades of yellow are produced by the metadiamidobenzene. The solution is sufficiently concentrated when a distinct color appears after a lapse of one or two minutes.

Place 100 cc. of the properly diluted solution in one of the cylinders. Into the others measure 0.1-, 1.0-, and 2.0-cc. portions of the standard solution of nitrite and fill with water to the 100-cc. marks. Add to each of the four cylinders 1 cc. of sulphuric acid and 1 cc. of the metadiamidobenzene. Stir the contents of each cylinder with a separate glass rod. Place in tubes of white paper — made by wrapping strips of filter paper about the cylinders and fastening them with pins — and set them on a white surface.

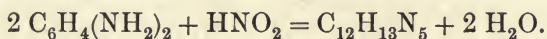
After about 20 minutes compare the color in the solution to be tested with that of the standards. If, as will probably be the case, the color falls between those of two of the standards, empty all the tubes and repeat the experiment with other standards containing quantities of nitrite ranging between the limits previously established. Proceed in this manner until a standard is obtained in which the color is identical with that of the solution to be tested.

The colors are compared by looking downward through the tubes. The depth of the color increases with time; the metadiamidobenzene must therefore be added to the solution to be tested and to the standards as nearly simultaneously as possible. Much time may be saved by using graduated cylinders with side tubes

near the bottom which are furnished with stopcocks — so-called “Hehner cylinders.” Only two of these are required for a determination, since the darker liquid can be drawn off until the colors — on looking through them in a downward direction — appear to be identical. The concentration of the solutions so compared is inversely proportional to their vertical height.

When two solutions are compared with respect to the intensity of their color, care should be taken to bring both of them into the same relation to the light. If the shades of color in two tubes appear to be identical, the positions of the tubes should be exchanged and the shades again compared.

The colored compound which is produced when nitrous acid and metadiamidobenzene are brought together is triamidoazobenzene:



The reaction is so delicate that one can determine by means of it 0.03 of a milligram of N_2O_3 in a liter of water. The eye distinguishes most accurately the shades of color which are developed in solutions containing from 0.03 to 0.3 of a milligram of N_2O_3 per liter. The colorimetric method is mainly employed for the determination of nitrous acid in excessively dilute solutions, as in contaminated well or spring waters. For more concentrated solutions the permanganate method is used. If colored waters are to be examined by this process, they must first be decolorized. For this purpose, 200 cc. of a hard water are treated with 3 cc. of a sodium carbonate solution (1 : 3) and 0.5 cc. of caustic soda (1 : 2); while soft waters are treated with a few drops of an alum solution. If this treatment fails to precipitate the coloring matter, the method cannot be used.

Another process for the colorimetric determination of nitrous acid in very dilute solutions is that known as Trommsdorf's. It is based on the reaction which takes place when zinc iodide and nitrous acid are brought together. The iodine which is liberated — and indirectly the nitrous acid — is estimated by the blue color imparted to starch paste.

EXERCISE XXVII

COLORIMETRIC DETERMINATION OF AMMONIA

THE DETERMINATION OF "FREE" AND "ALBUMINOID" AMMONIA
IN WATER BY THE METHOD OF WANKLYN,
CHAPMAN, AND SMITH

The following reagents are required:

1. A large supply of water which is free from ammonia. To obtain this, the ordinary distilled water is acidified with sulphuric acid and redistilled. The first portion of the distillate must be rejected because it contains the ammonium salts which have collected on the glass within the condenser and the receiver. Water which has been purified in this manner must be used in making up all the reagents and in all operations in which the use of water containing ammonia can affect the results of a determination.

2. A solution of Nessler's reagent. To prepare this, dissolve 8.75 grams of potassium iodide and 3.25 grams of mercuric chloride in 200 cc. of boiling water. When a clear solution is obtained, add drop by drop a cold saturated solution of mercuric chloride until a slight permanent precipitate of mercuric iodide appears. Dissolve in the solution 40 grams of potassium hydroxide or 30 grams of sodium hydroxide. When cold, add a little more of the mercuric chloride and dilute to 250 cc. Allow the solid matter to subside and then pour the clear liquid into a bottle having a good stopper. The reagent should be used from a smaller bottle which is filled from the larger supply as occasion requires. The solution should have a light yellow color. If it is colorless, more mercuric chloride must be added. Its sensitiveness should be tested from time to time with very dilute solutions of ammonia.

3. Two standard solutions of ammonium chloride, one containing 1 milligram of NH_3 in each cubic centimeter, and the other one-hundredth as strong. The first is obtained by

dissolving 3.1370 grams of pure ammonium chloride in water and diluting to a liter; and the second, by diluting 10 cc. of the first solution to a liter.

4. A solution of potassium hydroxide and potassium permanganate. To prepare this, dissolve 100 grams of the former and 4 grams of the latter in half a liter of water and distill off 125 cc. Dilute the residue to half a liter with water free from ammonia.

5. A boiled saturated solution of sodium carbonate. For the practice determination, a specimen of a water known to be impure or one which has been rendered impure by the addition of sewage should be employed.

Place 500 cc. of the water to be tested in a well-cleansed tubulated liter retort. If the water is soft, or if it has an acid reaction, add 10 cc. of the sodium carbonate solution. Attach the retort to a clean condenser and distill over into a measuring flask 200 cc. of water. Replace the receiver with a 150-cc. measuring flask. Introduce 50 cc. of the alkaline permanganate solution into the retort and continue the distillation until the receiver is filled to the mark.

It remains to determine colorimetrically the ammonia in the two distillates. The first contains the "free" ammonia, or that which was already formed in the water; and the second, the "albuminoid" ammonia, or that which was produced by the action of the alkaline permanganate on the nitrogenous organic matter.

To a 10-cc. portion of the first distillate, in a narrow test tube, add 1 cc. of the Nessler reagent. Stir with a glass rod and observe the color which is developed. If, after waiting for a few minutes, the color is found to be only a light shade of pure yellow, the solution is not too concentrated. If, on the other hand, red is detected in the color, measured portions of the distillate must be diluted with measured quantities of water until a solution is obtained in which the reagent will produce no red whatever. Determine the ammonia exactly as nitrous acid was determined in the preceding experiment, using 2 cc. of the Nessler reagent in each cylinder.

Proceed with the distillate containing the "albuminoid" ammonia in precisely the same manner.

The results should be stated in milligrams of ammonia per liter of the original water, or parts per million.

Regarding the significance of so-called "free" and "albuminoid" ammonia in drinking water, see Wanklyn's *Water Analysis*.

EXERCISE XXVIII

THE DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS

I. BY KJELDAHL'S METHOD

The following reagents and apparatus will be required for one or another of the various modifications of the method :

1. Half a liter of pure concentrated sulphuric acid, to which 100 grams of phosphorus pentoxide have been added.

2. Metallic mercury or the oxide of mercury. The latter is prepared by pouring a hot solution of mercuric chloride into a hot solution of potassium hydroxide. The commercial oxide usually contains nitrogen and cannot be used.

3. Finely ground potassium permanganate.

4. A nearly saturated solution of caustic soda.

5. A solution of potassium sulphide made by dissolving 40 grams of the commercial sulphide and diluting to a liter; or by dissolving an equivalent quantity of the hydroxide in water, dividing the solution into two equal parts, saturating one of these with hydrogen sulphide and adding the other to it. The strength of the solution should be determined by titrating into a solution containing a known weight of mercury until the liquid blackens a paper moistened with lead acetate.

6. Granulated zinc, also zinc dust.

7. Phenolsulphuric acid made by dissolving 50 grams of phenol in enough concentrated sulphuric acid to make 100 cc. of the solution.

8. Pure sodium thiosulphate.
9. A one-tenth normal solution of ammonia.
10. A one-fifth normal solution of sulphuric acid.
11. A pear-shaped flask with long neck, known as a Kjeldahl digestion flask.
12. A 500- or 600-cc. flask from which to distill the ammonia.
13. A Peligot tube in which to absorb the ammonia.
14. A condenser with an inner tube of block tin.
15. A glass tube from 150 to 200 mm. in length, having a diameter about equal to that of the tin tube and a bulb in the middle from 30 to 35 mm. wide. One end passes through a stopper which fits the distillation flask, while the other end is attached to the tin tube of the condenser with a piece of rubber tubing.
16. A sifter for the potassium permanganate. This is made by slightly enlarging the end of a glass tube of suitable size and binding over it a piece of very fine wire gauze.

a. By Wilfarth's Modification of Kjeldahl's Method

(Not applicable to nitro-compounds or to nitrates)

Weigh from 150 to 175 milligrams of pure uric acid into the digestion flask. Add 0.7 gram of the mercuric oxide or 0.6 gram of mercury. Measure in 20 cc. of the sulphuric acid to which phosphorus pentoxide has been added. Fasten the flask in an inclined position over a wire gauze (under a hood), and heat with a Bunsen burner, gently at first, but afterwards for an hour and a half to the boiling point of the liquid.

In the case of most organic compounds the acid blackens in consequence of the separation of carbon, and then becomes lighter in color as the oxidation progresses. The black gives way by degrees to a dark brown, a light brown, and a light yellow color, and finally the liquid becomes colorless. The disappearance of all color from the acid is usually regarded as an indication of the complete conversion of the nitrogen into ammonia;

but in the case of uric acid, either the acid does not blacken at all or it becomes colorless before the reaction is finished. When the light yellow stage is reached, the oxidation is usually assisted by sifting in a little of the pulverized permanganate, though in most cases such assistance is unnecessary.

Place the flask in a vertical position and introduce minute quantities of the permanganate by tapping the sifter on the side or top until the liquid assumes a green or purplish color. Place about 200 cc. of water in the distilling flask and pour the contents of the digestion flask slowly into it. Wash the latter and add the washings to the liquid in the former. Measure 50 cc. of the standard acid into the absorption tube and attach it to the condenser. Having made ready to close the distillation flask and to connect it with the condenser, cautiously neutralize the sulphuric acid with the strong alkali. When it is believed that the neutral point has been nearly reached, add at once a considerable excess of the alkali, also about one and a half times the quantity of the potassium sulphide which is required to precipitate the mercury. Throw in a few pieces of granulated zinc and quickly close the flask. Distill off from 150 to 200 cc. of the liquid and determine the excess of acid in the Peligot tube by means of the standard solution of ammonia.

To ascertain whether any portion of the ammonia has been derived from the reagents, make a blank determination, using half a gram of pure sugar in the place of the uric acid.

b. Gunning's Modification of Kjeldahl's Method

(Not applicable to nitro-compounds or to nitrates)

Weigh two 5-cc. portions of well-mixed milk into digestion flasks and evaporate to dryness in a water or air bath. Treat each of the residues with 10 grams of powdered potassium sulphate and 20 cc. of concentrated sulphuric acid. Place funnels in the necks of the flasks and cover them with watch glasses. Heat cautiously until frothing ceases, and then more strongly

until the acid becomes colorless. Complete the determination as directed under *a*, omitting the addition of potassium permanganate and sulphide. A blank determination should be made in order to ascertain to what extent the results are to be corrected for ammonia in the reagents.

c. Jodlbauer's Modification of Kjeldahl's Method

(Applicable to nitro-compounds and nitrates)

Weigh from 300 to 500 milligrams of pure potassium nitrate into a digestion flask. Add to it 2.5 cc. of the phenolsulphuric acid and 20 cc. of the sulphuric acid which has been treated with phosphorus pentoxide; also from 2 to 3 grams of zinc dust and five drops of the ordinary platinum chloride solution. Heat until the acid becomes colorless, and then proceed as directed under *b*.

d. Foerster's Modification of Kjeldahl's Method

(Applicable to nitro-compounds and nitrates)

Treat from 300 to 500 milligrams of potassium nitrate with a six per cent solution of phenol in strong pure sulphuric acid, adding 3 cc. for each tenth of a gram of the nitrate. Shake the flask lightly, without heating, until the nitrate is dissolved, and then introduce at one time from 1 to 2 grams of sodium thiosulphate. When the reaction which follows is finished, measure in a quantity of the strong sulphuric acid equal to two-thirds the volume of phenolsulphuric acid which was first added. Pour in half a gram of mercury and heat until the contents of the flask become colorless. Finish the determination as directed under *a*.

Instead of phenolsulphuric acid, a solution of salicylic acid in sulphuric acid (1:30) may be used.

Gunning's method is also modified so as to apply to nitrates. The material is treated in the digestion flask with 30 cc. of sulphuric acid containing 1 gram of salicylic acid. The contents

are thoroughly mixed and frequently shaken for a period of ten minutes. Five grams of sodium thiosulphate and 10 grams of potassium sulphate are added. The mixture is heated gently until frothing ceases, and then more strongly until it is nearly colorless. The determination is finished as directed under *b*.

The object in using phenol and salicylic acid in the case of nitrates is to convert the nitric acid into nitro-derivatives of these substances, and the reducing agents—zinc and sodium thiosulphate—are employed to convert the nitro-derivatives into amido-compounds which are decomposed by concentrated sulphuric acid with conversion of all of the nitrogen into ammonia.

II. BY DUMAS' METHOD

Select a piece of hard glass tubing having an internal diameter of 15 or 16 mm. and a length greater than that of the combustion furnace by about 150 mm. Smooth the rough ends in the flame of the blast lamp, and fit each with a perforated stopper through which a small glass tube has been passed. At a point within the tube about one-third of its length from one end, place a short roll of copper wire gauze to serve as a partition. Fill the longer space to within 100 mm. of the end of the tube with coarse copper oxide and confine it in its place by inserting a short roll of copper wire gauze. Fill the shorter space in the same manner with fine copper oxide. Insert the stoppers and heat the tube in the furnace, raising the temperature gradually to a full red heat. Pass a slow current of oxygen through the tube for an hour and a half, or a somewhat more rapid current of air for a longer time. Cut off the oxygen or air and pass carbon dioxide through for an hour or more. Cool the copper oxide very slowly and uniformly in the current of carbon dioxide, and when it is cold close the tube at both ends with short pieces of rubber tubing and glass plugs. Both the oxygen (or air) and the carbon dioxide will be sufficiently purified

by passing them through a saturated solution of acid sodium carbonate and then over calcium chloride.

Select for the combustion a hard glass tube with an internal diameter of 15 or 16 mm. and a length about equal to that of the furnace. Smooth the rough edges of one end and draw out the other to a small tube about 100 mm. long. When finished, each end should project 50 or 60 mm. beyond the furnace. The large end of the tube is to be closed with a tightly fitting perforated rubber stopper in which is inserted a small glass tube so bent that it can be joined conveniently to a Schiff's azotometer. The smaller end of the combustion tube is to be connected with an apparatus for the generation of carbon dioxide.

The azotometer, Fig. 52, in which the nitrogen is collected, is to be filled with mercury to a point somewhat above the place where the gas enters, and beyond that point with a concentrated solution (1.35 sp. gr.) of caustic potash. The apparatus is not to be connected with the combustion tube until nearly all of the air has been expelled from the latter.

To fill the tube, introduce:

1. A loose plug of ignited asbestos.
2. A layer, about 125 mm. in length, of small pieces of native magnesite previously dried at 150°.
3. A short roll of oxidized copper wire gauze.
4. A layer of coarse copper oxide, 50 mm. in length.
5. A layer of fine copper oxide, 75 mm. in length.
6. A small platinum boat containing not more than 200 milligrams of pure uric acid.
7. Enough fine copper oxide to cover the boat. The acid and the fine oxide, after the introduction of the latter, are to be well mixed with a stiff wire, the end of which has been formed into a spiral resembling that of a small corkscrew.

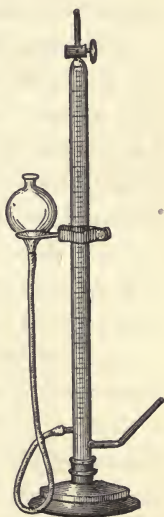


FIG. 52

8. A layer of fine copper oxide, 75 or 100 mm. in length. This is introduced without removing the mixing wire, and in it the wire is cleansed from any of the acid which may adhere to it.

9. Enough coarse copper oxide to fill the tube to within 250 mm. of the end.

10. A roll of copper gauze, 125 mm. in length, and thick enough to fill the tube. This must be freed from oxide by heating to redness in the flame of the blast lamp and dropping it while hot into a test tube containing half a cubic centimeter of pure methyl alcohol. The tube is immediately closed with a cork to protect the hot copper from the air. Afterwards it is heated to 130° in an air bath and then placed in a desiccator until needed. The metallic copper serves to reduce any oxides of nitrogen which are formed during the combustion.

11. A layer of coarse copper oxide, 50 or 75 mm. in length, to burn any carbon monoxide which may possibly be formed by reduction of the dioxide, if the metallic copper contains iron.

12. A short roll of wire gauze to keep the last portion of copper oxide in place.

Place the filled tube in the furnace and immerse the end of the outlet tube in a small quantity of mercury. Attach to the other end of the combustion tube an apparatus for the generation of carbon dioxide. The best arrangement for this purpose is a short combustion tube filled with small pieces of magnesite. To prepare this, a tube about 350 mm. in length is closed at one end, filled with the carbonate, and drawn out at the other end to permit its being attached by means of rubber tubing. It is well to cover the magnesite tube by slipping over it a cylinder of sheet iron made by rolling and hammering the metal upon an iron rod of the proper diameter. The covered tube need not be placed in a furnace, but may be rested upon the ring of an iron stand. Any other apparatus for the generation of carbon dioxide may be used, provided it is in a condition to yield the gas free from air, which is not the case with the ordinary Kipp apparatus. It is to be remembered in this

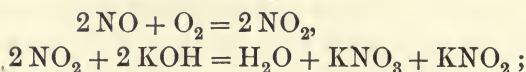
connection that the gas obtained by dissolving marble in acids always contains air, and that neither boiling the marble under water nor exhausting with the pump suffices to liberate the imprisoned gas.

Having joined the two tubes, heat the one containing the magnesite (throughout its whole length, but most strongly at the rear end) until a quite rapid current of carbon dioxide is obtained. When it is believed that all the air has been expelled from the apparatus, connect it with the azotometer and allow the gas to ascend through the caustic potash. After a few minutes, open the stopcock and force out the small quantity of gas which collects at the top. Close it again and observe whether the gas which now enters the measuring tube is completely absorbed. If it is not, or if the quantity of air which collects at the top is sufficient to affect the results appreciably, lower the reservoir and let the caustic potash run into it by opening the stopcock. Continue to heat the magnesite and repeat the test for air from time to time until a satisfactory result is obtained.

Pinch the rubber connecting the two tubes and detach the rear one, inserting in its place a tightly fitting glass plug. Light the burners under the copper oxide last introduced and under the roll of wire gauze, and when these have been brought to a full red heat, light the burner under the oxide nearest the magnesite. Advance slowly and from both ends with the heating until all of the copper oxide except that in the vicinity of the substance to be burned, as well as the roll of gauze, is at a red heat, and then heat the remaining oxide, gently at first and afterwards strongly, until the combustion is complete. Finally, heat the magnesite in the rear end of the tube until all of the nitrogen has been driven into the azotometer tube.

To measure the gas, connect the azotometer by means of a narrow glass tube with a second one filled with water, and transfer the nitrogen to the latter in order that its volume may be read over water instead of over caustic potash, whose vapor tension will, of course, be unknown.

If the surface of the metallic copper in the front portion of the tube was in good condition, i.e. free from oxide, and if the combustion was properly managed, the gas will be free from nitric oxide. Otherwise it may be present, and the volume, therefore, too large. The presence of nitric oxide in nitrogen may be detected, and its quantity approximately determined in the following manner: The azotometer containing the gas over the alkali is connected with a second one containing some air over water. Having ascertained the volumes of both gases under atmospheric pressure, a few cubic centimeters of air are introduced into the nitrogen. If the latter contains nitric oxide, it will be converted into the dioxide which will then be absorbed by the alkali. The azotometer is shaken and the gas again measured. If contraction takes place, i.e. if the final volume is less than the sum of the volumes of the nitrogen and of the air introduced, it is due to the reactions



and the volume of the nitric oxide is equal to two-thirds of the contraction which follows the introduction of the air, while the volume of the nitrogen in it is one-half as large. Finally, the gas is measured over water by transferring it to the azotometer from which the air was taken. A correction must, of course, be made for the oxygen which has disappeared in converting the NO into NO₂. When the air is passed from the azotometer containing water into that containing the alkali, a slight contraction takes place owing to diminished aqueous tension; hence the method is not adapted to the detection and determination of minute quantities of nitric oxide.

The following modification of the Dumas method is to be preferred when an efficient Sprengel pump is available: A combustion tube of suitable length and diameter is closed at one end. A few small pieces of magnesite are dropped into it and confined in place by a plug of asbestos. In all other respects the tube

is filled in the usual manner. The open end is then drawn out to a small tube 70 or 80 mm. in length. After laying the filled tube in the furnace, it is connected with the pump by means of thick rubber tubing securely tied with waxed shoemaker's thread. The tube is pumped out and meanwhile the rubber connection is covered occasionally with a thin coat of shellac. When a sufficient vacuum has been obtained, the magnesite is heated until the pressure within the tube is restored. A gas measuring tube filled with a solution of caustic potash is then inverted over the outlet of the pump, and the combustion conducted as usual. After it is finished the temperature is lowered very slowly and uniformly until the glass becomes sufficiently rigid, when the burner under the magnesite is closed and the tube pumped out.

III. BY VARRENTRAPP AND WILL'S METHOD

(Ruffle's Modification)

There are required :

1. A combustion tube with an internal diameter of 18 mm. and a length of 575 mm. One end is to be drawn out to a small tube and then closed.

2. A Peligot tube in which to absorb ammonia. The absorption tube and the combustion tube are each fitted with a perforated stopper and are connected by a small glass tube.

3. Standard solutions of sulphuric acid and ammonia. Those used in the Kjeldahl process will suffice.

4. A mixture of equal parts by weight of dry calcium hydroxide and of finely powdered sodium thiosulphate which has been dried at 100°.

5. A mixture of equal parts by weight of finely powdered sugar and flowers of sulphur.

6. Granulated soda-lime.

To fill the combustion tube, introduce :

- (a) A loose plug of asbestos which has been ignited over the blast lamp.

(b) A layer of the lime-sulphur mixture 25 to 30 mm. in length.

(c) The substance mingled with the mixtures 4 and 5. Weigh out a quantity of any nitrogenous commercial fertilizer which will yield from 35 to 60 milligrams of nitrogen, and mix it thoroughly with from 5 to 10 grams of the sugar-sulphur mixture. Pour upon a glazed paper or into a porcelain mortar a quantity of the lime-thiosulphate mixture which will fill the tube for a length of 250 mm. Add to this the mixture containing the substance to be analyzed. Mix thoroughly and pour the whole into the combustion tube. Rinse the paper or mortar with a little of the lime-thiosulphate mixture, and shake down the contents of the tube.

(d) Introduce enough soda-lime to fill the tube to within 50 or 60 mm. of the end, and finally a plug of previously ignited asbestos.

Hold the tube in a horizontal position and tap with it on the table until a sufficient channel for the escape of gas is produced along its whole length. Place the tube in the furnace with the end projecting far enough to insure the safety of the stopper. Connect it with the absorption apparatus and measure into the latter 50 or 75 cc. of 0.2 normal sulphuric acid.

Bring the front portion of the soda-lime to a full red heat; then beginning with the burner nearest the heated part of the tube, light at intervals the others in their order until the combustion of the substance begins. Burn slowly, but finally bring the whole tube to redness. When the liquid in the absorption apparatus rises in the limb towards the furnace, attach the aspirator, break off the small end of the combustion tube, and draw air through the apparatus for a few minutes. Determine the excess of the acid with tenth-normal ammonia, using cochineal as the indicator.

This modification of the Varrentrapp-Will method is applicable to nitro-compounds and nitrates. In its original form the substance was decomposed by soda-lime only, and the application of the method was therefore limited to those substances in which the nitrogen is not in combination with oxygen.

CHAPTER XII

PHOSPHORUS AND ARSENIC

EXERCISE XXIX

THE DETERMINATION OF PHOSPHORIC ACID IN PHOSPHATE ROCK

There are required :

1. A nitric acid solution of ammonium molybdate, which may be prepared from molybdenum trioxide or from the commercial ammonium molybdate. (a) To prepare it from the former, dissolve 25 grams of the trioxide in 104 cc. of ammonia of 0.96 specific gravity, and pour the solution, slowly and with constant stirring, into 312 cc. of nitric acid of 1.2 specific gravity. Or, (b) dissolve 37.5 grams of pulverized commercial ammonium molybdate in 250 cc. of hot water, and pour the solution, as directed above, into 250 cc. of nitric acid of 1.2 specific gravity. The solution prepared from the trioxide contains about 5 per cent of molybdic anhydride, while that prepared from the ammonium salt will contain a quantity of the anhydride ranging between 5.5 (for $(\text{NH}_4)_2 \text{MoO}_4$) and 6.1 per cent (for $(\text{NH}_4)_6 \text{Mo}_7 \text{O}_{24} \cdot 4 \text{H}_2\text{O}$), according to the composition of the salt employed. Whether the solution is prepared in the one way or the other, it should be allowed to stand for several days in a moderately warm place in order that any phosphoric acid which it contains may be precipitated. The clear solution is afterwards decanted, or siphoned off, and kept in a dark place. Exposed to the light, it is slowly decomposed with deposition of yellow crystals having the composition $\text{MoO}_3 \cdot 2 \text{H}_2\text{O}$. Fifty cubic centimeters of the reagent are added for each decigram of P_2O_5 to be precipitated.

Owing to the high cost of molybdenum compounds, it is desirable to recover the molybdic acid which has been employed in precipitating phosphoric acid. To do this, the filtrates and the precipitates containing it are evaporated to dryness and heated until nearly all of the ammonium nitrate has been decomposed. The residue is digested with ammonia, filtered, and the filtrate treated with magnesia mixture (see 2, below). After standing for 12 hours, the ammonium magnesium phosphate is filtered off, the filtrate acidified with nitric acid, and the anhydride collected upon a filter and washed with the least possible quantity of cold water.

2. "Magnesia Mixture." Dissolve 27.5 grams of crystallized magnesium chloride, $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$, in water. Add 175 cc. of ammonia of 0.96 specific gravity and dilute to a liter. Allow the solution to stand for some days, and then filter, if necessary. Of this solution 10 cc. are to be added for each decigram of P_2O_5 to be precipitated.

Treat from 4 to 5 grams of finely powdered phosphate rock in a porcelain dish with 60 cc. of concentrated hydrochloric acid. Digest on a water bath for an hour and then evaporate to dryness. Moisten the residue with strong hydrochloric acid, again evaporate to dryness, and finally heat for an hour at 110° . This treatment will render the silica anhydrous and insoluble. Add 10 cc. of nitric acid of 1.2 specific gravity and evaporate to dryness. Repeat the treatment with nitric acid and the subsequent evaporation until all hydrochloric acid is removed. Digest the residue for a considerable time on the water bath with water containing 10 cc. of dilute nitric acid. Filter into a half-liter measuring flask, wash the residue and the paper with water, and dilute the filtrate to the mark.

To 25-cc. portions of the phosphoric acid solution add 75 cc. of the molybdate reagent. Warm for six hours at a temperature of 50° . Take out a small portion of the clear liquid, add to it an equal volume of the molybdate solution, and warm for some time at 50° . If a precipitation of phosphoric acid follows,

add more molybdate to the main solution and continue to heat for several hours at 50°. When the precipitation is found to be complete, filter through a small paper. Wash the precipitate, without attempting to bring all of it upon the paper, with a solution consisting of 10 parts of the molybdate, 2 parts of nitric acid (1.2 sp. gr.), and 8 parts of water, until the filtrate gives no reaction for calcium when treated with a little sulphuric acid and twice its volume of alcohol. Instead of the solution given above, one of 25 grams of ammonium nitrate in 250 cc. of water may be used to wash the precipitate. Dissolve the precipitate in the beaker and on the filter in the least possible quantity of dilute ammonia by passing a small quantity of the liquid through the paper repeatedly until a perfect solution is obtained. Dilute the filtrate with a little water and pass it again through the paper into a 200-cc. beaker. Wash the beaker in which the phosphoric acid was precipitated, and the filter with dilute ammonia (1 part of ammonia to 3 parts of water). Add dilute hydrochloric acid until the precipitate begins to dissolve somewhat slowly on stirring the liquid, and then add from 6 to 8 cc. of ammonia (0.96 sp. gr.). Let the solution, whose volume at this stage should not exceed 70 or 75 cc., cool to the temperature of the room. Add from a burette, slowly and with constant stirring, from 15 to 20 cc. of the magnesia mixture, and then a quantity of ammonia (0.96 sp. gr.) equal to about one-third of the volume of the liquid in the beaker. After six hours collect the precipitate on a filter, using the filtrate to bring into the paper the portion which clings to the glass. Wash with a solution of 1 part of ammonia (0.96 sp. gr.) in 3 parts of water until the filtrate gives no reaction for chlorine. Dry the filter and remove the precipitate to a weighed porcelain crucible. Burn the paper in a platinum wire. Heat the crucible for some time over a Bunsen burner and then two or three minutes over the blast lamp. If the material, after ignition, is not perfectly white in color, add a few drops of nitric acid, evaporate to dryness, heat over a

Bunsen burner, and then again over the blast lamp. Treat the filtrate with more magnesia mixture in order to ascertain whether the precipitation was complete. Dissolve the precipitate in hydrochloric acid. If the solution is cloudy, silica is probably present, and its weight must be determined and deducted from the apparent weight of the pyrophosphate. For this purpose filter, wash thoroughly with water containing a little hydrochloric acid, and burn the paper in a weighed platinum crucible. Finally, in order to ascertain whether any molybdenum was precipitated with the phosphoric acid, treat the acid solution of the pyrophosphate with hydrogen sulphide.

The composition of ammonium phosphomolybdate is given by Rammelsberg as $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_{11} \cdot 6 \text{H}_2\text{O}$, but according to Hundeshagen (*Zeitschrift für analytische Chemie*, **28**, 14), the compound, however precipitated, has the composition $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_{12}$, when dried at 130° . Precipitated from a nitric or hydrochloric acid solution and undried, it is said to hold in loose combination two molecules of these acids and one of water. The substances whose presence should be avoided in solutions from which phosphoric acid is to be precipitated by ammonium molybdate are: (1) arsenic and silica, which may also be precipitated; (2) all compounds which, like hydriodic acid and many organic compounds, reduce molybdic acid; (3) organic acids, such as tartaric and citric, in the presence of which the precipitation is incomplete; (4) hydrochloric acid and chlorides which dissolve the precipitate to some extent even in the presence of an excess of ammonium molybdate. The phosphomolybdate is also somewhat soluble in water and in dilute nitric and sulphuric acids, but its solubility in these is greatly diminished by the presence of an excess of ammonium molybdate. It is for this reason that the latter is added to the water with which the precipitate is washed. Its solubility is likewise lessened by the presence of ammonium nitrate, hence

the frequent use, for economical reasons, of a ten per cent solution of this salt as a wash liquid.

Ammonium magnesium phosphate, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, loses five molecules of water at 100° . At higher temperatures it is converted into magnesium pyrophosphate with loss of water and ammonia. It is soluble in 15,300 parts of water at ordinary temperatures (Fresenius), but nearly insoluble in water containing 2.5 per cent of ammonia (NH_3). Its solubility is in all cases increased by ammonium chloride, but to a less extent in the presence of an excess of magnesia mixture. The conversion of the salt into magnesium pyrophosphate should be effected in a porcelain, and not in a platinum, crucible.

Metaphosphoric and pyrophosphoric acids and their salts must be converted into orthophosphoric acid or orthophosphates before attempting to precipitate with ammonium molybdate or with magnesia mixture. This transformation may be effected in two ways: (1) by long-continued fusion with 4 or 6 parts of potassium sodium carbonate; and (2) by warming for a long time with a strong mineral acid. The first method is applicable only to those metaphosphates and pyrophosphates which are completely decomposed by fusion with alkaline carbonates. In other cases — those, for example, of the metaphosphates and pyrophosphates of the alkaline earths — the second method must be employed.

EXERCISE XXX

THE DETERMINATION OF PHOSPHORUS IN IRON BY THE STOECKMANN-FRESENIUS METHOD

Treat about 5 grams of pig-iron drillings in a liter flask, in the neck of which a funnel has been placed, with 60 cc. of nitric acid of 1.2 specific gravity, adding the acid in small portions from time to time and heating the flask. When the frothing ceases, boil the liquid gently until the iron is dissolved. Transfer the contents of the flask, together with the rinsings,

to a 200-cc. porcelain dish and evaporate to a small volume. Add 5 grams of ammonium nitrate and continue the evaporation to dryness on a sand bath, stirring the contents of the dish from time to time. Heat the dried residue over the naked flame until the carbon is burned and the ammonium nitrate is destroyed. Digest with hot concentrated hydrochloric acid until the iron oxide is dissolved. Dilute, filter out the silica, wash the paper, and evaporate the filtrate repeatedly with nitric acid until all the hydrochloric acid has been removed. Precipitate the phosphoric acid, first with ammonium molybdate and then with magnesia mixture, as directed in Exercise XXIX. The ammonium-magnesium phosphate may contain arsenic. To remove this, dissolve in a little hydrochloric acid, heat the solution to 70° , and treat with hydrogen sulphide. Filter, wash the paper, concentrate the filtrate, and precipitate the phosphoric acid by adding the requisite amount of ammonia and a little magnesia mixture. Proceed with the precipitate as directed in the preceding exercise.

If the residue of silica (see above) is not white, fuse it, together with the filter ash, with sodium carbonate, dissolve with dilute nitric acid, and proceed in the same manner as with the nitric acid solution of the iron, i.e. evaporate with ammonium nitrate, digest the residue with hydrochloric acid, filter, evaporate with nitric acid, precipitate with ammonium molybdate, etc.

EXERCISE XXXI

THE DETERMINATION OF PHOSPHORIC ACID IN FERTILIZERS

(Method of the Association of Official Agricultural Chemists)

The reagents required are:

1. Ammonium molybdate, prepared as directed in Exercise XXIX.

2. Magnesia mixture, prepared as directed in Exercise XXIX. It may also be made by dissolving 5.5 grams of recently ignited

magnesium oxide in dilute hydrochloric acid (avoiding an excess of the latter), boiling the solution for a few minutes with a small additional quantity of the oxide to precipitate iron, aluminium, and phosphoric acid, filtering, adding 70 grams of ammonium chloride and 175 cc. of ammonia of 0.96 specific gravity, and diluting with water to half a liter.

3. Dilute ammonia, prepared by adding 1 part of ammonia of 0.96 specific gravity to 3 parts of water, or 1 part of concentrated ammonia to 6 parts of water.

4. A solution of ammonium nitrate, prepared by dissolving 50 grams of the salt in water and diluting the solution to half a liter.

5. A solution of ammonium citrate, made by dissolving 92.5 grams of citric acid in 375 cc. of water, nearly neutralizing with ammonia, cooling, adding ammonia until the solution is exactly neutral (using a saturated alcoholic solution of corallin as the indicator), and finally diluting to half a liter. The solution should have a specific gravity of 1.09 at 20°.

6. A solution of magnesium nitrate, made by dissolving 80 grams of calcined magnesia in nitric acid, avoiding an excess of the latter, boiling the solution with a small excess of magnesium oxide, filtering, and diluting to half a liter.

a. Determination of the Water-Soluble Phosphoric Acid

Place 2 grams of the well-mixed and finely pulverized fertilizer in a filter 90 mm. in diameter, and wash with successive small portions of water, allowing each portion to pass through the paper before adding another, until the volume of the filtrate is 250 cc. If the filtrate is turbid, add a little nitric acid. Dilute to any convenient volume, mixing well, and determine the phosphoric acid, as directed below, in measured portions of the solution which correspond to 0.5 gram of the original material. To the hot liquid add 50 cc. of ammonium molybdate for each decigram of P_2O_5 supposed to be present. Digest at

65° for one hour. Filter and wash the precipitate with the ammonium nitrate solution 4. Add more ammonium molybdate to the filtrate and digest again at 65° to determine whether the precipitation is complete. Dissolve the precipitate on the filter with ammonia and hot water. Wash into a beaker to a volume not exceeding 100 cc. Nearly neutralize with hydrochloric acid. Cool and add magnesia mixture from a burette at the rate of one drop per second, stirring vigorously. After 15 minutes add 30 cc. of ammonia of 0.95 specific gravity. Allow the beaker to stand for two or three hours, then collect the precipitate on a filter and wash it with the dilute ammonia 3. Transfer the precipitate to a weighed porcelain crucible, burn the paper, and ignite, first over the Bunsen burner and finally for ten minutes over a blast lamp.

b. Determination of the Citrate-Insoluble Phosphoric Acid

Measure 100 cc. of the ammonium citrate solution 5 into a strong 200-cc. flask, and place the flask, loosely stoppered, in a warm water bath. When the temperature of the solution has risen to 65°, drop into it the paper containing the water-insoluble phosphate. Close the flask tightly with a smooth rubber stopper and shake violently until the filter paper is reduced to a pulp. Return the flask to the bath and maintain the temperature of the citrate solution at exactly 65°, shaking the flask every five minutes. At the expiration of one-half hour from the time of introducing the paper, remove the flask and filter its contents as rapidly as possible. Wash the residue thoroughly with water having a temperature of 65°. Transfer the filter with its contents to a crucible and ignite until all organic matter is destroyed. Digest the residue with from 10 to 15 cc. of strong hydrochloric acid until the phosphate is dissolved. Dilute to 200 cc. and determine the phosphoric acid in measured portions of the solution, as directed under *a*, i.e. by precipitating first with ammonium molybdate and then with magnesia mixture,

etc. Instead of burning off the organic matter, as directed above, it may be destroyed by one of the methods given under *c*.

In the case of "non-acidulated goods," the removal of the water-soluble phosphoric acid may be omitted. If, as in bone, fish, etc., considerable animal matter is present, the residue, after treatment with ammonium citrate, is to be freed from organic matter by one of the processes given under *c*.

c. Determination of Total Phosphoric Acid

To destroy the organic matter, treat 2 grams of the material by one of the following methods.

1. Evaporate with 5 cc. of the magnesium nitrate solution 6. Ignite, and dissolve the residue in hydrochloric acid.

2. Boil with from 20 to 30 cc. of strong sulphuric acid, adding from 2 to 4 grams of sodium nitrate at the beginning of the digestion, and another small portion when the liquid has become nearly colorless, or adding the nitrate in small portions from time to time. A Kjeldahl flask graduated to 250 cc. is recommended for the digestion. When the solution has become colorless, add 150 cc. of water, boil for a few minutes, cool, and dilute to the mark with water.

3. Digest with strong sulphuric acid and such other reagents as are used in the Kjeldahl or the Gunning method for the determination of nitrogen. Do not add potassium permanganate, but when the solution has become colorless, add about 100 cc. of water and boil for a few minutes. Cool and dilute to any convenient volume. This method is advantageous when both the phosphoric acid and the nitrogen are to be determined in a fertilizer.

4. Dissolve in 30 cc. of concentrated nitric acid, adding a little hydrochloric acid.

5. Add 30 cc. of strong hydrochloric acid, heat, and treat cautiously from time to time with small quantities of pulverized potassium chlorate.

6. Dissolve with from 15 to 30 cc. of strong hydrochloric acid and with from 5 to 10 cc. of concentrated nitric acid. This method is recommended for fertilizers containing considerable iron or aluminium phosphate.

Boil until all phosphates are dissolved and all organic matter is destroyed. If hydrochloric or sulphuric acid has been used as a solvent, add 15 grams of ammonium nitrate. Cool and dilute to 200 or 250 cc. Mix well and filter through a dry paper. Measure off portions of the filtrate corresponding to 0.25 or 0.5 gram of the original material, neutralize with ammonia, and dissolve with nitric acid any precipitate which appears. Determine the phosphoric acid in the usual manner.

The citrate-soluble phosphoric acid is the difference between the total and the sum of the water-soluble and the citrate-insoluble acids, and the "available" phosphoric acid is the sum of the water-soluble and the citrate-soluble acids.

d. "Optional Volumetric Method" for the Determination of Phosphoric Acid in Fertilizers

The required reagents are :

1. A molybdic solution prepared as previously directed. To each 100 cc. of it add 5 cc. of nitric acid of 1.42 specific gravity. This solution should be filtered each time before using.

2. Potassium nitrate or ammonium nitrate solution for washing. To prepare this, dissolve 3 grams of the salt in 100 cc. of water.

3. Nitric acid for washing. Dilute 100 cc. of nitric acid of 1.42 specific gravity to a liter.

4. A standard solution of potassium hydroxide free from carbonate, which contains 18.17106 grams of KOH in a liter. One cubic centimeter of it should neutralize 0.3238 cc. of a normal acid, and is equivalent to 1 milligram of P_2O_5 .

5. A standard solution of nitric acid equivalent to that of potassium hydroxide, or one-half as concentrated. Phenolphthalein is to be employed as the indicator.

6. An alcoholic solution of phenolphthalein.

A part of the solution made as directed under *c* may be employed for the determination.

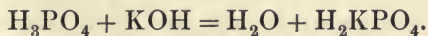
For percentages of 5 or below, use a volume corresponding to 0.4 gram of the substance; for percentages between 5 and 20, use a volume corresponding to 0.2 gram of the substance. If the percentage of phosphoric acid is above 20, use a volume corresponding to 0.1 gram of the material.

Add from 5 to 10 cc. of nitric acid or an equivalent quantity of ammonium nitrate, nearly neutralize with ammonia, dilute to from 75 to 100 cc., and heat in the water bath to 60° or 65°. Add 25 or 35 cc. of filtered ammonium molybdate, according as the percentage of phosphoric acid is below or above 5. Stir, and allow to stand for fifteen minutes. Filter immediately thereafter, wash once or twice by decantation (using from 25 to 30 cc. of water each time, agitating the precipitate thoroughly, and allowing it to settle), and then transfer to the filter. Wash five or six times with water, or until the entire filtrate reaches a volume of 200 cc. Transfer the filter with its contents to a beaker, dissolve in a small excess of the standard potassium hydroxide, add phenolphthalein, and titrate with the standard nitric acid.

*Other Volumetric Methods for the Determination of
Phosphoric Acid*

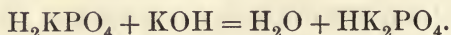
Free phosphoric acid may be determined by means of a standard alkali, with use of methyl orange or phenolphthalein, or, better, with use of both of these indicators.

If alkali is added to a solution containing the free acid and methyl orange, the color changes from red to yellow with the formation of the di-hydrogen salt,



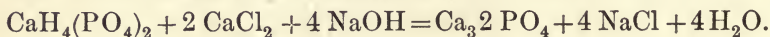
In other words, the di-hydrogen phosphates are neutral to methyl orange.

If phenolphthalein is subsequently added to the solution and the titration with alkali is continued, the red color of this indicator appears only after the conversion of the di-hydrogen phosphate into the mono-hydrogen salt,

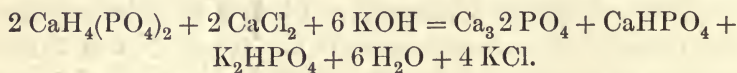


It will be seen that these reactions may be employed for the determination of the phosphoric acid in the phosphates of the alkalis; for, if to a solution containing such a salt and methyl orange a mineral acid is added, the red color of the indicator will appear only when all of the phosphate has been converted into the di-hydrogen salt, and this may then be titrated with a standard alkali and phenolphthalein.

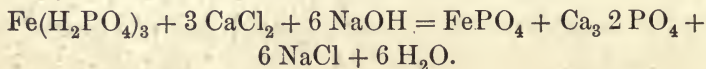
With certain modifications, the method is likewise applicable to the determination of phosphoric acid in the phosphates of the alkaline earths, magnesium, iron, aluminium, etc. The liquid containing the phosphate in solution and an excess of the acid in which it was dissolved is treated with methyl orange and then carefully neutralized with potassium or sodium hydroxide, leaving the phosphoric acid in the form of di-hydrogen phosphate. There are then added phenolphthalein, an excess of calcium chloride, and finally a standard alkali until the red color of the indicator appears. The reactions which take place may be represented by the equation



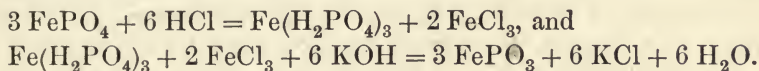
The precipitate may be redissolved and the determination repeated. The addition of an excess of calcium chloride is essential, since otherwise the reactions are in part as follows:



The reaction which takes place when the phosphoric acid is in combination with iron or aluminium may be represented as follows:

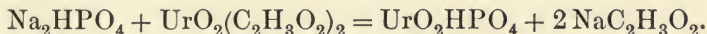


The same relative quantity of alkali is required for the precipitation of the phosphoric acid as in the case of phosphates free from iron and aluminium. If the phosphoric acid is wholly in the form of the iron or aluminium salt, the addition of calcium chloride, before titrating with a standard alkali and phenolphthalein, is unnecessary; for



Another method still in use for the volumetric determination of phosphoric acid is based on the fact that the uranyl salts precipitate the acid in the form of a phosphate of definite composition, which is not decomposed by potassium ferrocyanide, and which does not therefore give with that reagent the characteristic color reaction of uranium salts.

If uranyl acetate is added to a solution of a phosphate containing no other free acid than acetic acid, the reaction which follows may be represented by the equation



If ammonia or ammonium salts are present, the precipitate has the composition $\text{UrO}_2\text{NH}_4\text{PO}_4$, in which the ratio of Ur_2 to PO_4 is the same as in the salt UrO_2HPO_4 . Both salts are insoluble in acetic acid, and neither gives a color reaction with potassium ferrocyanide.

In practice, the solution of the phosphate is treated with sodium acetate to insure the neutralization of any free mineral acid which may be present, and then with the standard solution of uranyl acetate until a drop of the liquid, removed with a glass rod and brought into contact with a drop of potassium ferrocyanide solution upon a porcelain plate, gives the color reaction. It is better, however, to proceed with the titration until a strong color reaction is obtained, and then to titrate back with a standard solution of some phosphate. The solution of ferrocyanide must be freshly prepared; and since the color

reaction is retarded by certain substances, the conditions under which the solutions are standardized should be, as nearly as possible, like those which it is known will prevail in the subsequent work. The uranyl salt (acetate or nitrate) may be standardized against microcosmic salt, if only alkaline bases are in combination with the phosphoric acid to be determined. If, however, as usually happens, the phosphoric acid is combined with calcium, the uranyl solution must be standardized against calcium phosphate. This precaution is rendered necessary by the fact that uranyl phosphate is inclined to carry down with it a small quantity of calcium phosphate. The difficulty may also be overcome by titrating the solution of calcium phosphate into a measured quantity of the standard uranyl solution until the liquid no longer gives the color reaction with potassium ferrocyanide. The uranium method is excluded in the case of phosphates containing iron or aluminium, owing to the insolubility of the phosphates of these metals in acetic acid.

Other methods of more limited application than either of the foregoing are based on the precipitation of phosphoric acid (1) by lead salts, and (2) by silver salts.

(1) The solution, which must be free from chlorides and sulphates, is treated with sodium acetate to neutralize any nitric acid which may be present, and then with the standard solution of lead acetate until no further precipitation occurs. Or, better, the solution of phosphate to which sodium acetate has been added is treated with more than a sufficient quantity of the lead salt, and the excess is titrated with a standard solution of potassium chromate until the liquid gives a red color with neutral silver nitrate.

(2) The solution, which should be as nearly neutral as possible, is treated with an excess of a standard silver nitrate. After careful neutralization of the liquid with ammonia, and filtration, the excess of the silver is determined by the method of Mohr or by that of Volhard.

Two indirect volumetric methods for the determination of phosphoric acid have been proposed. One of them is based on the reduction of uranyl phosphate or uranyl-ammonium phosphate with zinc and an acid, and its reoxidation with a standard solution of potassium permanganate, while the other depends on a similar reduction and reoxidation of the molybdophosphate of ammonium.

The Determination of Phosphorus in Organic Compounds

The preliminary treatment by which the phosphorus to be determined is converted into phosphoric acid and the organic matter destroyed by oxidation is similar to or identical with that employed in the determination of sulphur in organic compounds.

If the compound is not volatile, it may be decomposed by the method of Liebig, or it may be heated in a glass tube with a mixture of 1 part of potassium chlorate and 8 parts of dry sodium carbonate (Kolbe's method. See Fresenius, *Quantitative Analyse*, 2, 74). Volatile compounds may be treated advantageously by the method of Carius or by that of Sauer.

If the solution of phosphoric acid obtained by any of the foregoing methods contains no metals except those of the alkalis, the acid may be precipitated directly by magnesia mixture and determined as magnesium pyrophosphate. If other metals are present, the acid must be precipitated by ammonium molybdate, dissolved in ammonia, and then reprecipitated by magnesia mixture.

When organic substances containing phosphorus are incinerated in the usual manner, a portion of the phosphorus is lost by volatilization notwithstanding the presence of ash-forming (non-volatile) bases. The same is true of sulphur, chlorine, and the alkalies. Hence when animal or vegetable matter is reduced to an ash with a view to determining its inorganic constituents, special methods of incineration must be employed.

The Separation of Phosphoric Acid from Other Substances

The fact that most phosphates are insoluble in neutral and alkaline solutions, while nearly all of them are dissolved by acids, renders the separation of phosphoric acid from bases and from other acids somewhat difficult. In many cases it is better first to precipitate the substances from which it is to be separated, and then to determine the acid in the filtrate. The following list includes the reagents most frequently employed in the separation of phosphoric acid.

1. *Ammonium Molybdate* separates the acid from all bases except molybdenum and ammonia, but not from silica and arsenic acids. If silica is present, the material should be repeatedly evaporated to dryness with strong hydrochloric acid, the residue heated for some time at 110° , and then evaporated with nitric acid until all the hydrochloric acid has been removed. The filtered solution will be free from silica. Owing to the danger of converting the acid phosphates into the pyro- or meta- salts, the residue should not be heated above 110° . Arsenic should be removed by treating the acid solution with hydrogen sulphide. If there are present silver, lead, mercury, copper, cadmium, bismuth, or any other metals which are precipitated from acid solutions by hydrogen sulphide, it is well to remove them before precipitating the phosphoric acid with ammonium molybdate.

The precipitate of ammonium phosphomolybdate is, in all cases, to be dissolved in ammonia, the ammoniacal solution treated with magnesia mixture, and the phosphoric acid finally determined as magnesium pyrophosphate.

2. *Mercurous Nitrate* separates phosphoric acid from all bases except mercury. It also precipitates meta- and pyrophosphoric acids. The phosphate is dissolved in a moderate excess of nitric acid and the solution treated in a porcelain dish with a quantity of mercury which is somewhat more than equivalent to the free nitric acid. The liquid is then evaporated to dryness on the water bath. The residue is repeatedly moistened

with water and evaporated until the vapors arising from the dish no longer contain nitric acid. Hot water is then added. The precipitate, which consists of mercurous phosphate, mercury, and mercurous oxynitrates, is collected upon a small filter, thoroughly washed and dried. The contents of the paper are transferred to a platinum crucible and mixed with dry sodium carbonate. The paper is rolled into a compact ball and buried under the carbonate in the crucible. The crucible is heated under a hood with a good draught, gently for half an hour and then to full redness. The contents of the crucible are dissolved in water, the solution filtered, if necessary, the filtrate slightly acidified with hydrochloric acid, and the phosphoric acid determined as magnesium pyrophosphate.

If the substance contains iron and aluminium, these are precipitated, in part at least, with the mercurous phosphate. The iron phosphate, however, — but not that of aluminium, — is decomposed by the subsequent fusion with sodium carbonate. If aluminium is present, the process is modified in the following manner: The substance is dissolved in the least possible quantity of nitric acid. The hot solution is then treated (1) with mercurous nitrate, (2) with a little mercuric nitrate, and (3) with caustic soda until a slight but permanent red precipitate appears. The precipitate, which now contains no aluminium, is to be treated in the manner previously described.

This method of separating phosphoric acid was devised by Rose. It is employed instead of the molybdate method when the presence of molybdenum would embarrass the subsequent separation of the bases.

3. *Tin Oxide* separates phosphoric acid from the metals of the alkaline earths, also from nickel, cobalt, manganese, zinc, aluminium, and from iron when present in small quantities (Reissig). For the details of the method, see Fresenius, *Quantitative Analyse*, 1, 406.

4. *Silver Nitrate* separates phosphoric acid from the fixed alkalies and from the alkaline earths. The material is dissolved

in water or in the least possible amount of nitric acid and the solution treated first with silver nitrate and then with silver carbonate to neutralize the excess of acid. The precipitate is collected upon a paper, washed, and dissolved in nitric acid. The silver is precipitated by hydrochloric acid, and the phosphoric acid by magnesia mixture.

5. *Lead Acetate* also separates phosphoric acid from the fixed alkalies and from the alkaline earths. The substance is dissolved in the least possible quantity of nitric acid and the solution treated (1) with a little ammonium chloride, (2) with lead acetate, and (3) with lead carbonate to neutralize the excess of acid. After long digestion the precipitate is collected on a paper, washed, and dissolved in a slight excess of nitric acid. The lead is then precipitated by sulphuric acid and alcohol, and the phosphoric acid by magnesia mixture.

6. In cases where it is desired to separate phosphoric acid from the alkalies and alkaline earths, rather than to determine it, the acid may be advantageously precipitated from the nearly neutral solution by ferric chloride and ammonium acetate.

7. *Hydrogen Sulphide* separates phosphoric acid from all those metals which are quantitatively precipitated by it from acid solutions. It is, however, generally preferred to precipitate lead by sulphuric acid and alcohol, and silver by hydrochloric acid.

8. *Ammonium Sulphide* separates cobalt, manganese, and zinc from phosphoric acid. The hydrochloric acid solution of these metals is placed in a flask and treated with tartaric acid, ammonium chloride, ammonia, and ammonium sulphide in excess. The flask is then closed and allowed to stand in a warm place until the liquid above the precipitate is clear and has a pure yellow color. The precipitate is collected on a filter and washed with water containing ammonium sulphide. The phosphoric acid in the filtrate may be precipitated with magnesia mixture without removing the excess of ammonium sulphide. Owing to the solubility of its sulphide in ammonium sulphide,

this method is not adapted to the separation of nickel from phosphoric acid.

9. *Sulphuric Acid* separates barium, strontium, calcium, and lead from phosphoric acid. The phosphates are dissolved in hydrochloric acid, or, if lead is present, in nitric acid, and the metals precipitated with a small excess of sulphuric acid. If strontium, calcium, or lead are to be separated, alcohol must be added to render the precipitation complete.

EXERCISE XXXII

THE DETERMINATION OF ARSENIC AS MAGNESIUM PYROARSENATE

Weigh about 0.3 gram of pure arsenious oxide into a 400- or 500-cc. flask. Add a little hydrochloric acid and a small quantity of potassium chlorate. Warm, and introduce from time to time other small portions of the chlorate until the liquid has a strong odor of chlorous acid. Afterwards continue to heat gently until the odor has nearly disappeared. Transfer the liquid to a beaker, make it strongly alkaline with ammonia, and add a moderate excess of magnesia mixture. Stir thoroughly and keep in a cold place for twenty-four hours or longer. Collect the precipitate on a paper filter, using small portions of the filtrate for the purpose, and wash with a mixture of three parts of water and one of ammonia until the filtrate no longer gives a reaction for chlorine. Dry at a temperature under 100° and remove the precipitate, without injuring the paper, to a small porcelain dish or a piece of glazed paper. Return the filter to the funnel. Moisten well with dilute nitric acid, and then, after fifteen or twenty minutes, wash out the paper with small portions of boiling water. Evaporate the filtrate in a weighed porcelain crucible on the water bath. Add the main portion of the precipitate and heat the crucible and its contents in the air bath to a temperature of 125° or 130° . Afterwards heat for two hours on a sand

bath, then for an equal length of time to a higher temperature on an iron plate, and finally over a lamp, with gradually rising temperature, to constant weight. The expulsion of the ammonia from the ammonium magnesium arseniate must be effected at comparatively low temperatures, otherwise some of the acid may be reduced with loss of arsenic.

The trioxide of arsenic, and arsenious compounds generally, cannot be heated with hydrochloric acid without loss except in the presence of a strong oxidizing agent.

Like phosphoric acid, arsenic acid may be precipitated by ammonium molybdate. The precipitate — ammonium molybdoarsenate — is soluble in ammonia, and from the ammoniacal solution the arsenic acid may be precipitated by magnesia mixture. It may also, like phosphoric acid, be precipitated quantitatively by uranyl acetate or nitrate.

When arsenic in solution is wholly in the arsenious condition, it may, with certain precautions, be precipitated as the trisulphide, collected upon a weighed filter, and dried to constant weight at 100° . Owing to the danger of contamination with free sulphur, it is, however, generally better to convert the sulphide into arsenic acid and to precipitate this finally with magnesia mixture.

CHAPTER XIII

SILICATES

Whatever the method employed to decompose a silicate, it must first be converted into a very fine powder, and the more refractory the substance is, the finer must be the powder. In all cases a high degree of subdivision greatly facilitates the decomposition. The material to be analyzed is usually reduced to a coarse powder by crushing it with a hammer upon a steel anvil or in a steel mortar and is then ground, a small portion at a time, in an agate mortar. The different small portions are well mixed in a watch glass or other suitable receptacle, and the material is then reground in the same manner. In order to remove any particles of steel which may have been detached, a magnet is passed back and forth through the powder before grinding it in the agate mortar. Porcelain and glass mortars should not be used when the substances to be pulverized are harder than ordinary salts. Substances having a hardness of 7 or more, i.e. equal to or higher than that of quartz, should not be ground even in agate. It is safer to pulverize them in steel mortars and to separate the finer from the coarser material by sifting. This operation, also that of elutriation, which is sometimes resorted to for the reduction of refractory substances, is described below.

1. *Sifting.* A piece of washed and well-dried linen is placed over the mouth of a stand cylinder and somewhat depressed in the center so as to form a baglike receptacle for the material to be sifted. The partially pulverized mineral is placed in the depression and the cylinder covered with a piece of soft leather. The latter is tightly stretched over the top and secured under the rim of the cylinder by tying it with a string or by grasping

it between the thumb and forefinger. The finer material is then forced through the sieve by tapping upon the leather cover. The coarser material which remains upon the cloth is reground and again sifted in the same manner. It is obvious that if the substance is not perfectly homogeneous, the grinding and sifting must be continued until the whole of the material has been passed through the cloth. The powder which collects in the bottom of the cylinder is well mixed before withdrawing a portion for analysis.

2. *Elutriation*. In this operation advantage is taken of the fact that when powdered substances are suspended in a liquid, the larger particles sink more quickly than the smaller ones. The material is ground with water in an agate mortar and transferred with the aid of a wash bottle to a beaker. Here it is stirred up with more water and then allowed to stand about one minute. The water, together with the finer material which remains suspended in it, is poured into another beaker, while the coarser material remaining in the bottom is reground and again elutriated. The regrinding of the sediment must, of course, be continued until the whole of the material has been reduced to a uniformly fine condition. When the water containing the elutriated substance has become perfectly clear, it is decanted and the residue is dried in the beaker and well mixed.

Since water dissolves to some extent, or attacks nearly all substances, especially when they are in a state of fine subdivision, the process of elutriation should not be resorted to unnecessarily.

THE DETERMINATION OF WATER IN SILICATES

If a silicate contains nothing volatile except water and does not absorb oxygen when heated in the air, the determination of water in it is very simple. It is then necessary only to ignite a weighed quantity of the material over the blast lamp and ascertain the loss in weight. On the other hand, the determination

is more difficult if the mineral contains iron in the ferrous condition or other oxidizable matter, or substances which, like chlorine, fluorine, boric acid, and the alkalies, are liable to form volatile compounds at or below the temperature required for the expulsion of the water. In such cases the mineral must be mixed with some substance which will decompose it and thus facilitate the liberation of the water and at the same time retain the otherwise volatile constituents. The water must then be collected in a weighed absorption apparatus. A few of the methods which are employed when the water in silicates cannot be determined by simple ignition are given below.

1. *Sipcoecz's Method*.* About 4 grams of finely powdered potassium-sodium carbonate are strongly heated in a platinum crucible and then allowed to cool to 60° or 50°. About 1 gram of the pulverized and dried silicate is thoroughly mixed with the carbonate with the aid of a platinum wire. The mixture is transferred to a roomy platinum boat and the crucible rinsed with a little of the dried carbonate. The boat is then placed in the middle of a porcelain tube which is glazed on the inside and has a length of 40 centimeters and an internal diameter of 17 mm. The porcelain tube is placed in a hot-air bath 25 centimeters in length in such a way that the two ends project equally. The ends are closed with perforated stoppers through which are passed short pieces of glass tubing. To one of these is attached a tube filled with calcium chloride, and to the other a gas-purifying apparatus consisting of a cylinder containing strong sulphuric acid and a tube filled with soda-lime. The latter is connected in turn with a gasometer filled with air. The temperature of the bath is raised to 120° or 130° and a moderately rapid current of air conducted through the apparatus for an hour. The porcelain tube is then placed in a combustion furnace and the calcium chloride tube replaced by a weighed U-tube containing glass beads which have been moistened with concentrated sulphuric acid. Air is again conducted through the apparatus and the

* *Zeitsch. anal. Chem.*, 17, 206.

temperature of the tube in the vicinity of the boat is raised very gradually to a full red heat. After maintaining this temperature for about an hour, the end of the tube nearest the absorption apparatus is cautiously heated in order to volatilize any water which may have condensed at that point. The U-tube is then detached and weighed.

If it is desired to use the same material for the determination of other constituents than water, the boat should be loosely covered with a lid which may be readily made for it from a piece of platinum foil.

2. *Jannasch's Method*.* The finely pulverized material is dried over calcium chloride, mixed with lead chromate, and heated in a combustion tube through which a current of dry air is passing. The water is collected and weighed in a U-tube containing calcium chloride. The combustion tube is given the same form as that usually employed in the determination of carbon and hydrogen in organic compounds. It is also cleansed, dried, and filled in the same manner and with the same precautions as when an organic compound is to be analyzed. The tube should have an internal diameter of 10 or 12 mm., a length of 46 or 47 centimeters, and a "bayonet" with a horizontal length of 12 centimeters. There are introduced (1) a roll of copper wire gauze 10 mm. in length; (2) a layer of coarse lead chromate, 100 mm.; (3) a layer of fine lead chromate, 15 mm.; (4) the mixture containing the substance, filling from 65 to 70 mm.; (5) fine lead chromate, 50 mm.; (6) coarse chromate, 180 mm.; (7) a roll of wire gauze, 10 to 20 mm. long. After filling the tube and tapping with it upon the table to produce a channel for the passage of air and water vapor, it is placed in a combustion furnace. To the front end is attached an apparatus consisting of a weighed U-tube containing calcium chloride, a soda-lime tube, and a small U-tube filled with pieces of potassium hydroxide. The bayonet is connected with an air-drying apparatus consisting of a cylinder filled with a mixture of calcium

* *Ber. d. d. chem. Ges.*, 22, 221.

chloride and potassium hydroxide, a cylinder containing strong sulphuric acid, and a third cylinder containing a solution of potassium hydroxide. The drying apparatus is in turn connected with an air gasometer. The remaining steps are the same as in the combustion of an organic compound in a current of air or oxygen.

3. *Chatard's Method*.* Only the main features of this process will be given here. For the details the original article must be consulted. A platinum boat containing the silicate, mixed with an alkaline carbonate if necessary, is inclosed in a cylinder of platinum foil, to prevent loss of material from spattering, and placed in a platinum combustion tube such as is employed in the determination of carbon in iron and steel. The combustion tube is joined at one end with an air-drying apparatus, and at the other with a weighed absorption apparatus for the collection of water. To avoid the error arising from the diffusion of hydrogen through platinum, the tube is wrapped with several layers of asbestos paper which has been soaked in a saturated solution of borax.

4. *The Lead Oxide Method*, which in some respects is more simple than processes 1, 2, and 3, suffices for the determination of water in most silicates, and has the additional advantage of leaving the material in good condition for the determination of the alkalis.

5. *The Borax Method*, which has been brought to a high state of perfection by Jannasch.†

EXERCISE XXXIII

THE DETERMINATION OF WATER IN SILICATES BY MEANS OF LEAD OXIDE

There are required:

1. A hard glass tube 40 to 45 centimeters long, with an internal diameter of 15 or 16 mm. One end of the tube is

* *Am. Chem. Jour.*, 13, 110.

† *Praktischer Leitfaden der Gewichtsanalyse*, p. 243.

drawn out so that a small rubber tube can be slipped over it. The other end is closed with a perforated rubber stopper through which is passed a short piece of glass tubing.

2. An air-drying apparatus consisting of a tube filled with soda-lime and a tube or cylinder containing glass beads moistened with concentrated sulphuric acid.

3. Weighed absorption tubes for the collection of water. U-tubes with ground-glass stoppers are recommended. They are to be filled from half to two-thirds full of glass beads which are afterwards moistened with concentrated sulphuric acid. The acid should be introduced with a pipette, care being taken not to allow any of it to come in contact with the lubricant used in connection with the stoppers, and the quantity of acid thus introduced should suffice only to fill the horizontal portion of the tubes. Three tubes are required.

4. A quantity of pure and dry lead oxide. This is prepared by treating a solution of pure lead nitrate with ammonium carbonate, filtering, washing with water containing a little ammonium carbonate until the filtrate gives no reaction for nitric acid, and heating the carbonate in a platinum dish to 300° or 400° on a sand bath. The dish *must not be heated over a naked flame*. The formation of some red oxide during the decomposition of the carbonate will do no harm. The oxide is to be tested for nitric acid and kept in a desiccator until required.

Mix in a platinum crucible, with the aid of a platinum wire or spatula, about one gram of finely pulverized tourmaline which has been dried in a desiccator with about three times its weight of the lead oxide. Transfer the mixture to a roomy platinum boat, using small portions of the oxide to cleanse the crucible. Place the combustion tube in a short furnace. Remove the stopper and insert the boat. Attach the drying apparatus, 2, to the end which is fitted with a stopper, placing the cylinder containing the beads next to the tube. To the other end of the combustion tube attach an unweighed U-tube containing glass beads moistened with sulphuric acid, bringing the glass ends

close together within the rubber connectors. To show the rapidity of the current, insert between the soda-lime tube and the gasometer a small U-tube containing a little mercury, and then pass air through the apparatus for half an hour at the rate of two bubbles per second. Now insert a weighed U-tube between the one previously used and the combustion tube, and conduct dried air through the apparatus for another half hour at the same rate as before. Remove the weighed tube, leaving the unweighed one connected with the combustion tube, and weigh. If the tube has gained sensibly in weight, return it to its place, add another cylinder containing beads moistened with sulphuric acid to the arrangement employed to dry the air, and pass air through the apparatus for another half hour. When the weight of the U-tube is found to be sufficiently constant, insert it between the air-drying apparatus and the combustion tube and attach the two remaining weighed U-tubes to the other end, protecting the last one from the moisture of the air by joining to it a cylinder or another U-tube containing beads and sulphuric acid. Pass air through the apparatus and heat the tube in the vicinity of the boat, raising the temperature gradually, until the glass shows signs of softening. Maintain this temperature for half or three-quarters of an hour, and if any water collects in the front part of the tube, drive it into the absorption apparatus by cautiously heating the places upon which it has condensed. Cool the tube slowly and gradually without interrupting the current of air, and leave it, after detaching the absorption tubes, fully protected from the moisture of the air. Only one of the three weighed U-tubes, i.e. that next to the exit end of the combustion tube, should show any increase in weight. After weighing, return the absorption tubes to their places and again heat the silicate as before.

The presence of nitrate in the lead oxide is a frequent source of error in this method of determining water in silicates. It is therefore recommended that a blank determination be made with a few grams of the oxide whenever a new portion of this reagent is prepared.

EXERCISE XXXIV

THE DECOMPOSITION OF A SILICATE WITH AN ALKALINE CARBONATE AND THE DETERMINATION OF THE SILICA

Mix in a platinum crucible, with the aid of a platinum wire or spatula, or a glass rod the ends of which have been made smooth by softening them in the flame, about 1 gram of finely pulverized orthoclase with from three to four times its weight of dry potassium-sodium carbonate which is free from silica. Pour a little of the carbonate upon a glazed paper, cleanse the mixing rod in it, and then transfer the material on the paper to the crucible. Cover the crucible with a concave lid, place it in a clean pipe-stem triangle, and heat for twenty minutes in the flame of a good Bunsen burner. Heat afterwards over the blast lamp, moderately for a time and later more strongly, until the evolution of carbon dioxide ceases and the fused material becomes transparent. Place the cooled crucible upon its side, also the lid, in a porcelain dish of convenient size, or better in a platinum dish, and add a little water. Cover the dish with a watch glass. Raise one side of the cover from time to time and introduce small quantities of hydrochloric acid with a pipette until the evolution of carbon dioxide ceases. Remove the cover, the crucible, and its lid, washing the material on each of them very carefully back into the dish. Warm the dish, with the cover on, until the carbon dioxide in solution has been expelled, and then evaporate to dryness, with the cover off, on the water bath. Moisten the residue with strong hydrochloric acid and again evaporate to dryness. If the material balls together, pulverize it with a platinum spatula. Repeat the evaporation with hydrochloric acid two or three times and then heat the dish for an hour in an air bath at a temperature of 110° . Treat the residue with a little strong hydrochloric acid, add water, and digest for half an hour on the water bath. Filter, and wash the silica with hot water until the filtrate yields no weighable residue on

evaporation. It is very difficult to distinguish small particles of silica upon a concave surface of white porcelain, and almost impossible, therefore, to determine whether a dish of this kind has been sufficiently cleansed. For this reason it is better to use a platinum dish for the liberation and dehydration of the silicic acid. Partially dry the silica and place the filter containing it, folded so as to occupy but little space, in a weighed platinum crucible. Turn the crucible on its side in a triangle and cautiously burn the paper to a white ash. Heat the silica for a time over a Bunsen burner, and then, with the crucible covered, to constant weight over a blast lamp.

The silica must be tested as to its purity. For this purpose treat it with 2 or 3 cc. of dilute sulphuric acid and 8 or 10 cc. of strong hydrofluoric acid, which leaves no weighable residue when evaporated and ignited on platinum. Evaporate to dryness on a sand bath or iron plate and ignite over a Bunsen burner. If there is a residue, repeat the treatment with sulphuric and hydrofluoric acids. If there is still a residue, it consists of sulphates or oxides of metals belonging to the original silicate, and the decomposition of the mineral was incomplete. If the bases in the silicate all form sulphates which are unstable at high temperatures, the true weight of the silica may still be found, notwithstanding the incomplete decomposition, by subtracting the weight of the highly heated residue from that of the material before treatment with hydrofluoric acid. If, on the other hand, a part of the bases, like the alkalis, form more stable sulphates, the experiment must be repeated with a new portion of the mineral. If the silicate contains titanitic acid, this also will be found in the residue after treatment of the silica with hydrofluoric and sulphuric acids.

The completeness of the decomposition of a silicate may also be tested by heating the silica for an hour in a platinum or silver dish with a solution of sodium carbonate, 6 cc. of a saturated solution of the carbonate and 12 cc. of water for each 0.1 gram of the silica. If there is an insoluble residue after such

treatment, this should be fused with a fresh but smaller portion of the alkaline carbonate.

The silica which is liberated from its salts by an acid is always hydrated, and in that condition is somewhat soluble in water. The evaporation with strong hydrochloric acid and the subsequent heating to 110° are for the purpose of dehydrating it and rendering it insoluble. The temperature to which it is heated must not, however, be raised much above 110° owing to the danger of recombination with the bases. The silicates so formed would doubtless be easily decomposed by acid, but the liberated silica would be more or less hydrated and therefore somewhat soluble.

OTHER METHODS OF DECOMPOSING SILICATES

1. DECOMPOSITION BY LEAD OXIDES

This method was proposed by Berthier in 1821* and again brought forward as a new method by G. Bong in 1878.† It appears, however, to have been but little used. The general disinclination to employ it is probably due to the common experience that platinum vessels when heated directly in a flame are often injured by lead compounds. Berthier proposed to remove this objection to his method by heating with a mixture of nitrate and carbonate of lead. When the modification of the method here given is employed, there is no danger of injuring the vessel in which the decomposition is effected, provided the silicate contains nothing which can reduce lead compounds. If the mineral contains organic matter or other reducing substances, the powder must be ignited in the air before mixing it with lead oxide.

The pulverized mineral is mixed with from two to three times its weight of the oxide, and the mixture transferred to a

* *Annales de Chimie et de Physique*, 2 Ser., 17, 28.

† *Bulletin de la Société Chimique*, Nouvelle Série, 29, 50.

platinum boat. The boat, which should be surrounded with two or three turns of platinum wire to keep it away from the glass, is placed in a combustion tube and heated in a short furnace for not less than an hour. If practicable, the temperature is raised to the fusing point of the mixture; if, however, it is impossible to effect a fusion, the heating is continued for two hours. The boat is placed in a platinum dish and treated with dilute nitric acid and enough water to prevent separation of lead nitrate. A gentle heat is applied, and when the material separates from the platinum the boat is removed and washed. After complete decomposition by the nitric acid has been effected, the contents of the dish are evaporated to dryness; the residue is then moistened with strong nitric acid and again evaporated. The evaporation should not take place on a common water bath owing to the danger of forming lead sulphate. It is better to heat the dish on a large sand bath or on an iron plate until but little liquid remains, and then in an air bath, open at the top, which is kept at a temperature below 110° . The residue is finally heated for an hour at 110° , moistened with nitric acid, treated with water, and again heated for an hour nearly to the boiling point of the liquid. The silica, after collection on the filter, is washed with water containing a very little nitric acid and determined in the usual manner. The atmosphere of the room in which the experiment is performed must, of course, be free from hydrogen sulphide and the vapors of all other sulphur compounds.

The method is an excellent one for the decomposition of silicates, and is to be especially recommended for those in which it is desired to determine the alkalies. The filtrate from the silica contains all the bases in the form of nitrates, and these, after the precipitation of the lead by hydrogen sulphide, may be separated and determined by the usual methods.

2. DECOMPOSITION BY BISMUTH OXIDE

A method quite similar to that of Berthier was proposed by Hempel.* It consists in fusing the silicate (0.5 gram) with a large quantity (10 grams) of bismuth subnitrate and decomposing the resulting basic silicate with strong hydrochloric acid. The mixture of subnitrate and silicate is mildly heated as long as red vapors are evolved, and then for ten minutes to its melting point. The fused mass is poured, while still liquid, into a platinum dish floating upon cold water. Here it is decomposed by strong hydrochloric acid and the silica rendered insoluble by evaporation to dryness. The residue is treated with hydrochloric acid, in which everything except silica is soluble, and filtered. The silica is washed with water containing hydrochloric acid and determined in the usual manner. To prepare the filtrate for a determination of the bases, it is diluted with water until the greater portion of the bismuth has been precipitated as oxychloride. The precipitate is filtered and washed, and the remainder of the bismuth is removed by treating the filtrate with hydrogen sulphide.

3. DECOMPOSITION BY HYDROCHLORIC ACID

Many hydrated silicates, especially those belonging to the zeolite section and some anhydrous ones, are, when in a finely divided condition, completely decomposed in open vessels by more or less prolonged treatment with concentrated hydrochloric acid. And many silicates which are ordinarily but slightly attacked by hydrochloric acid are easily decomposed by it after long ignition. The silicic acid which is liberated by the action of hydrochloric acid on silicates usually presents a gelatinous and semi-transparent appearance; though in the case of some species, and generally when the mineral has previously been dehydrated, it separates as a white, meal-like powder. A few

* *Zeitsch. anal. Chem.*, 20, 496.

easily decomposed silicates yield, when treated with dilute acid, a silicic acid which is wholly soluble in water. Both the gelatinous and the pulverulent forms of silicic acid are somewhat soluble in water and in dilute acids. It is therefore necessary in all cases, after decomposition of a silicate by hydrochloric acid, to dehydrate the silica by repeated evaporation with concentrated acid and by heating to 110° . The testing of the silica as to its purity, by means of hydrofluoric acid or sodium carbonate, is even more necessary when a silicate has been decomposed by an acid than when it has been fused with the alkaline carbonates or with lead oxide.

4. DECOMPOSITION BY ACIDS UNDER PRESSURE

Silicates which in open vessels are but slightly, or not at all, attacked by hydrochloric and sulphuric acids are readily decomposed by them when heated under pressure, as proposed by Mitscherlich.* About 1 gram of the finely pulverized material is placed in a tube of hard glass which has been closed at one end, and there treated with an excess of hydrochloric acid (25 per cent), or of sulphuric acid (3 parts of the concentrated acid and 1 part of water). The tube is then carefully sealed and heated for two hours in an iron tube at a temperature of 200° or 210° . The tube is strongly attacked by the acids; hence the method, though an effective one, for the decomposition of silicates cannot be employed when the substances to be determined are at the same time constituents of the glass.

This difficulty has been obviated and the method of Mitscherlich made generally applicable by Jannasch,† who places the silicate and the hydrochloric acid which is to decompose it in a platinum tube and incloses this in a tube of glass. The platinum tube has a length of 151 mm. and a diameter of 15 mm., and is provided with a cap through which passes a smaller tube

* *Journal für praktische Chemie*, **81**, 108; **83**, 455.

† *Ber. d. d. chem. Ges.*, **24**, 273; *Zeitsch. anal. Chem.*, **30**, 334.

having a length of 32 mm. and a diameter of 5 mm. The apparatus has a capacity of 26 cc. and weighs 57.5 grams. The powdered silicate is introduced through a funnel and treated with 10 cc. of hydrochloric acid (4 parts of strong acid to 1 part of water). The mineral and the acid are thoroughly mixed with a thick platinum wire, the end of which is bent to a loop. On removing the stirring wire it is rinsed back into the tube with 5 cc. of the acid. The platinum tube is closed and placed in one of glass which has an internal diameter of 22 mm. and a wall thickness not less than 2 mm. Acid is poured into the glass tube until the wider portion of the platinum tube is half submerged. The open end of the glass tube is drawn out before the blast lamp to a small diameter and the air in the apparatus expelled by inserting a narrow tube which is attached to a carbon dioxide generator. The tube is then sealed and heated for ten or twelve hours at a temperature of 190° or 210° . As there is no pressure in the tube when cold, the precautions usually observed in opening sealed tubes are unnecessary. The contents of the platinum apparatus are transferred to a platinum dish and treated in the usual manner. Notwithstanding the displacement of the air by carbon dioxide, the filtrate from the silica is generally found to contain a small quantity of platinum. This is to be removed by hydrogen sulphide before proceeding to a determination of the bases.

5. DECOMPOSITION BY HYDROFLUORIC ACID

A method very generally employed when the alkalis are to be determined is that proposed by Berzelius. It consists in the decomposition of the silicate by hydrofluoric acid and the conversion of the fluorides of the bases into sulphates. The pulverized material is treated in a platinum dish with a small quantity of fuming hydrofluoric acid and stirred with a platinum wire after each addition of the acid. After digesting for some time on a water bath at a temperature considerably below

the boiling point, a quantity of sulphuric acid (1 part of concentrated acid and 1 part of water) which is more than equivalent to the bases of the silicate is added. The contents of the dish are then evaporated, for a time on a water bath and later at a higher temperature, until the excess of the sulphuric acid has been expelled. The residue, when cold, is treated with strong hydrochloric acid, allowed to stand for some hours, and then dissolved in water. If the silicate contains no bases whose sulphates are insoluble, and the decomposition is complete, a clear solution will be obtained. If the solution is not clear, the insoluble matter must be treated with hydrofluoric and sulphuric acids in the same manner as the original material. The solution contains all the bases of the silicate as sulphates. The silica can, of course, be determined only indirectly. The hydrofluoric acid used in this experiment should yield no nonvolatile residue on evaporation. Owing to the poisonous nature of the vapors of hydrofluoric acid, the whole operation should be conducted under a good hood.

There are various modifications of Berzelius' method: (1) the material is moistened with dilute sulphuric acid and exposed for a long time in a lead box to the vapors of hydrofluoric acid which are generated by mixing fluor spar and concentrated sulphuric acid in the bottom of the vessel; (2) the mineral is heated in a platinum tube through which a current of dry gaseous hydrofluoric acid is passing; or (3) the silicate is decomposed by heating it with ammonium fluoride, with acid potassium fluoride, or with a mixture of sodium fluoride and acid potassium sulphate.

A method of decomposing silicates by hydrofluoric acid for the purpose of determining ferrous iron will be given in a later chapter.

6. DECOMPOSITION BY BARIUM HYDROXIDE AND CARBONATE

Formerly silicates were often decomposed by heating them with the hydroxide or carbonate of barium. The first compound attacks platinum, rendering the use of silver crucibles

necessary, and it nearly always contains alkali, while the second requires for its effective action a very high temperature, — a temperature so high, in fact, that the alkalies in the silicate are likely to be lost by volatilization. Hence these methods, though variously modified from time to time to remedy their defects, have been almost wholly abandoned.

Fusion with calcium carbonate has also been recommended (Deville).

7. DECOMPOSITION BY AMMONIUM CHLORIDE AND CALCIUM CARBONATE

For the method of Lawrence Smith, see *Zeitschrift für analytische Chemie*, **11**, 85. It consists in heating the silicate in a platinum crucible of special form with a mixture of calcium carbonate and ammonium chloride. The process is a simple one and in the case of many silicates is quite effective.

EXERCISE XXXV

THE DETERMINATION OF SILICON IN IRON

The treatment of the iron for the estimation of silicon is precisely the same as for the estimation of phosphorus, and a single portion of the material may, therefore, be made to serve for the determination of both elements.

Proceed as directed in Exercise XXX until the residue containing the silica has been collected and washed. Dry it, burn the paper, and mix the impure silica and the ash in a platinum crucible with about four times its weight of potassium-sodium carbonate, adding a little potassium nitrate. Proceed with the mixture as directed in Exercise XXXIV. Having found the weight of the silica plus that of any impurities it may contain, treat with hydrofluoric and sulphuric acids as previously directed and deduct the weight of the nonvolatile residue. The silica derived from iron often contains titanium oxide, hence this correction of its weight should never be omitted.

THE SEPARATION OF SILICA FROM OTHER SUBSTANCES

By the fusion of silicates, or substances containing silica, with the alkaline carbonates, and the subsequent treatment of the fused mass with hydrochloric or nitric acid, etc., silica is quantitatively separated from all the bases, leaving the latter, with the exception of the alkalis, in condition to be separated and determined by the usual methods.

By fusion with lead oxide and subsequent treatment with nitric acid, etc., silica is separated from all bases, leaving the alkalis, as well as all the other bases ordinarily occurring in silicates, in condition to be determined. The presence of lead in the filtrate containing the bases of the silicate does not greatly complicate their separation, provided none of them are precipitated from acid solutions by hydrogen sulphide.

Decomposition with hydrofluoric and sulphuric acids effects a complete separation of silica from all metals.

Decomposition with hydrochloric acid, when complete, together with the evaporation with strong hydrochloric acid, separates silica from all bases, leaving them in the best possible condition for determination.

The separation of silica from some of the acid-forming elements in such a manner that the latter may also be determined is more difficult than its separation from the bases. The substances whose presence in silicates gives rise to analytical difficulties which render necessary some modifications of the ordinary methods are (1) chlorine, (2) fluorine, (3) boron, (4) sulphur, (5) titanium. Owing to the volatility of hydrochloric, hydrofluoric, and boric acids, and of sulphur compounds, excepting sulphuric acid, a part or the whole of the first four of these elements is lost in rendering the silica anhydrous; while the fifth, titanium, always remains with the silica after dehydration. For the methods which are to be followed in the analysis of silicates containing these elements, the handbook of Rose should be consulted.

CHAPTER XIV

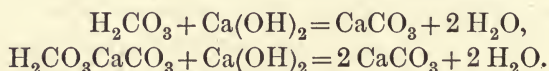
THE DETERMINATION OF CARBONIC ACID

EXERCISE XXXVI

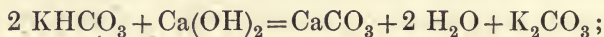
I. THE VOLUMETRIC DETERMINATION OF FREE AND SEMI-COMBINED CARBONIC ACID IN WATER

PETTENKOFER'S METHOD

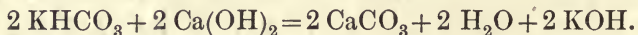
In its simplest form the method consists in the addition to the water of a measured but excessive quantity of a standard solution of barium or calcium hydroxide, and the determination of the excess by means of a standard solution of oxalic acid. The following equations will illustrate the reactions which are expected to take place when the water contains only free carbonic acid and acid carbonates of the alkaline earths:



Suppose, however, as often happens, that the water contains acid carbonates of the alkalis. The reaction which will then occur is represented by the equation

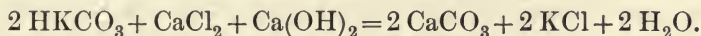


or, if an excess of the hydroxide is added, by the equation

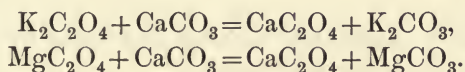


It will be observed that the alkalinity of the water, found by subsequent titration with an acid, is the same whether one or two molecules of the hydroxide are added for each molecule of the acid carbonate of an alkali. It will also be noticed that

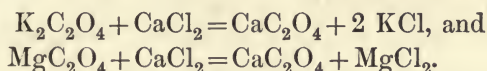
the semi-combined carbonic acid is correctly determined only when for every molecule of an acid carbonate of an alkali *not less* than two molecules of the hydroxide have been added. All danger of error from this source is avoided by adding to the water or to the standard solution of hydroxide a quantity of neutral calcium or barium chloride; for



There is also avoided, by such addition of a chloride, the error resulting from the presence in the water of substances which, like the soluble sulphates, precipitate the metals of the alkaline earths. A further advantage to be gained by the presence of the chloride is the prevention of a possible reaction between the oxalates of the alkaline metals or of magnesium on the one hand and calcium carbonate on the other, by which calcium oxalate and the carbonates of the alkalies and of magnesium are formed.



These carbonates, if formed, would neutralize a quantity of the standard oxalic acid; in other words, they would increase the apparent alkalinity of the solution. In the presence of a chloride of an alkaline earth no such irregularity can occur, since



If the water contains salts of magnesium, ammonium chloride must also be added in order to prevent the precipitation either of the carbonate or of the hydroxide of that metal. The former subsides very slowly, while the precipitation of the latter diminishes the alkalinity of the solution.

The excess of the calcium hydroxide cannot be immediately determined, since freshly formed calcium carbonate is amorphous and somewhat soluble in water, imparting to the latter an alkaline reaction. On standing, the amorphous compound

becomes crystalline and insoluble. The transformation is hastened by heat. The application of heat is, however, inadmissible when the solution contains ammonium salts. Freshly precipitated barium carbonate, on the other hand, is insoluble, but any advantage which might on this account be expected from the use of a standard solution of barium hydroxide, rather than one of calcium hydroxide, is lost when the water, as is usually the case, contains either the carbonate or the sulphate of calcium.

There are required :

1. A saturated solution of calcium hydroxide, which is prepared by slaking lime from marble, agitating the product with water, and allowing the suspended matter to subside. Filtration should not be attempted.

2. A standard solution of oxalic acid of such strength that each cubic centimeter is equivalent to 1 milligram of carbonic anhydride.

3. A solution of calcium chloride (1 part of the crystallized salt in 5 parts by weight of water).

4. A solution of ammonium chloride (1 part of the salt in 8 parts of water).

5. A sensitive solution of litmus.

Determine how much of the standard oxalic acid is required to neutralize 45 cc. of the calcium hydroxide solution. Place 100 cc. of a water having considerable "temporary hardness" (ordinary hydrant water will usually suffice) in a clean and dry flask. Add 3 cc. of the calcium chloride, 2 cc. of the ammonium chloride, and 45 cc. of the calcium hydroxide solution. Close the flask with a rubber stopper, shake, and then set it aside for twelve hours. Withdraw 50 cc. of the liquid and titrate with the standard oxalic acid, using litmus as the indicator. Repeat the titration with a second 50-cc. portion of the liquid. Instead of litmus, turmeric paper may be employed to detect the neutral point, in which case the acid is added until a drop of the liquid taken out upon a glass rod and placed upon the paper no longer

produces a brown ring. If the water contains only slight quantities of magnesium salts, ammonium chloride need not be added. This omission would be of advantage because in the absence of ammonium salts, phenolphthalein, which is much more sensitive than litmus or turmeric, could be used as the indicator.

The volume of the oxalic acid required to neutralize 50 cc. of the liquid is to be multiplied by 3 and the product subtracted from the volume which neutralizes 45 cc. of the calcium hydroxide solution. The difference is the number of milligrams of free and semi-combined carbonic anhydride in 100 cc. of the water. It is at the same time the number of parts by weight of the anhydride in 100,000 parts of the water, in which form the quantitative results of a water analysis are usually stated.

Another 100-cc. portion of the same water should be titrated with a standard solution of hydrochloric acid, using tropæolin or methyl orange as the indicator. The acid consumed will be equivalent to the *combined* carbonic acid if, as is probably the case, the water contains no other basic substances than carbonates.

If the quantity of free and semi-combined carbonic acid exceeds that of the combined, the difference between the two amounts is the *free* carbonic acid which was in the water.

II. THE DETERMINATION OF TOTAL CARBONIC ACID IN WATER

Briefly stated, the method consists in (1) the precipitation of the carbonic acid by calcium hydroxide, (2) the decomposition of the carbonate by hydrochloric acid, and (3) the collection of the carbonic acid in a weighed quantity of potassium hydroxide.

The calcium hydroxide is prepared by adding water to freshly and thoroughly burned lime until it falls into a fine dry powder. This is preserved in bottles having tightly fitting stoppers. The hydroxide always contains carbonate, and, since this cannot be separated, the carbonic acid must be determined in a weighed

average sample of the material. Owing, however, to the lack of uniformity in the distribution of the carbonate throughout the hydroxide, the correction of the results by means of such a determination is a matter of some uncertainty. It is for this reason that the use of any unnecessary excess of the hydroxide is avoided. If the water contains alkaline carbonates, calcium chloride must also be added in order to insure a complete precipitation of the carbonic acid. The slight solubility of calcium carbonate in dilute solutions of the hydroxide is a source of some error in the method. A compensating, and probably more than equivalent, error results from the unavoidable exposure to the air of the alkaline material during filtration.

The determination is made in the following manner: A flask holding somewhat more than 300 cc. is graduated to contain that amount, supplied with a tightly fitting rubber stopper, and weighed. There is then introduced a quantity of calcium hydroxide ranging from 0.5 gram to 3.0 grams, according to the amount of carbonic acid to be determined, after which the flask is closed and again weighed. The flask or other receptacle containing the water under investigation is placed in ice water or a freezing mixture and cooled nearly to zero. When sufficiently cold, the water is transferred by means of a siphon to the flask containing the calcium hydroxide. The quantity so transferred is ascertained by again weighing the flask. The weighing cannot, however, be made until the temperature of the water has risen to that of the balance room, owing to the condensation of atmospheric moisture upon the glass. After weighing, about 1 cc. of calcium chloride solution (1 to 10) is introduced. The flask is closed, shaken, and then heated for three-quarters of an hour upon a water bath to render the calcium carbonate crystalline and less soluble. When the solid matter has sufficiently subsided, the greater portion of the liquid above it is quickly filtered through a paper, with the least possible disturbance of the material in the bottom of the flask. The filter and its contents are then returned, without washing, to

the flask which still retains the greater portion of the carbonate. The remaining steps are the same as in Exercise XXXVII.

If the water can be taken directly from a large supply, as, for instance, from a spring, it is better to proceed in the following manner: The weighed flask containing the calcium hydroxide is provided with a doubly perforated rubber stopper carrying two small glass tubes of equal length. One of these ends just below the stopper, and the other near the lower end of the neck. The upper end of the former is closed with the finger and the flask is immersed in water. On removing the finger the water enters the flask through one tube while the air escapes through the other.

It frequently happens that the carbonic acid in bottled waters which have been saturated with the gas under pressure is to be determined. The plan usually adopted in such cases is that proposed by Rochleder.* A cork borer is pierced with a small drill at a distance from its cutting end somewhat greater than a cork's length. The other end of the borer is closed with a stopper in which there is a glass tube bent to a right angle. To this is attached a rubber tube which is supplied with a screw pinchcock to regulate the flow of the gas. The free end of the rubber tube is attached to the absorption apparatus described in Exercise XXXVII. The metallic tube is then bored into the stopper by turning the bottle until the small hole appears below the cork. When the gas ceases to flow a second and smaller hole is bored in the cork. Through this is pushed a glass tube until the end within the bottle is only slightly above the surface of the water. Air freed from carbonic acid is then aspirated for a few minutes through the whole apparatus in order to remove the gas which remains in the bottle above the water and in the tubes leading to the absorption apparatus. If the absorption tubes in which the carbonic acid is collected are now weighed, the quantity of gas held in the water by "over-pressure" will be ascertained.

* *Zeitsch. anal. Chem.*, 1, 20.

The carbonic acid remaining in the water in the bottle is determined in the manner already described, i.e. a siphon is inserted and a portion of the water transferred to a weighed flask containing a known quantity of calcium hydroxide, etc.

EXERCISE XXXVII

DETERMINATION OF CARBONIC ACID IN CARBONATES

I. BY ABSORPTION IN A WEIGHED QUANTITY OF SODA-LIME

The apparatus required consists of:

1. A flask having a capacity of from 150 to 300 cc. This is provided with a tightly fitting, doubly perforated rubber stopper, having in one hole a small dropping funnel with a glass stopcock and in the other a glass tube bent to a right angle. The stem of the funnel reaches nearly to the bottom of the flask, while the tube ends just under the stopper. The tube should be of sufficient diameter to allow the water which condenses in it to return to the flask. It is also well to cut or grind the end within the flask diagonally across the tube and to blow a bulb in the vertical limb just above the stopper. The tube serves to conduct the gas from the flask into the absorption apparatus. The funnel is employed for the introduction of the hydrochloric acid which is to decompose the carbonate, and through it also is conducted the air which is to displace the carbonic acid remaining in the flask when the decomposition is finished. It is closed at the top with a rubber stopper carrying a glass tube bent to a right angle.

2. A Geissler absorption apparatus partly filled with a solution of potassium hydroxide (sp. gr. 1.35). This is attached to the glass tube at the top of the dropping funnel by means of a rubber tube, and serves to remove the carbonic acid from the air which is aspirated through the flask.

3. A series of eight connected U-tubes which, for convenience, are designated by the letters *a*, *b*, *c*, *d*, *e*, *f*, *g*, and *h* in the order of their distance from the flask, 1. The tubes *a*, *b*,

and *c* have a height of 170 mm. and an internal diameter of 16 mm. The tubes *d*, *e*, *f*, *g*, and *h* are smaller, having a height of 110 mm. and a diameter of 12 mm. *a*, *b*, *c*, *d*, *g*, and *h* are closed with rubber stoppers; while *e* and *f*, in which the carbonic acid is absorbed and weighed, are closed with corks covered with sealing wax. It is better, however, to use for *e* and *f* glass-stoppered U-tubes with small side tubes, which are opened and closed by turning the stoppers. The whole system of tubes is suspended at a convenient height above the working table from hooks driven into a horizontal strip of wood. The tube *a*, which is nearest the flask, contains just enough calcium chloride to fill its horizontal portion; *b* is filled with calcium chloride; and *c*, with small pieces of pumice stone which have been soaked in a boiling concentrated solution of copper sulphate, and then dried and heated to a temperature sufficient to dehydrate the copper salt. Any vapors of hydrochloric acid escaping from the flask are absorbed in *c*. The tube *d* is filled with calcium chloride. The weighed tubes *e* and *f* are filled five-sixths full of coarsely granulated soda-lime and one-sixth full of calcium chloride, the latter being placed in both cases in the limb of the tube which is farthest from the flask. The tube *g* serves to protect *e* and *f* from the moisture and carbonic acid of the air. One limb, that toward *f*, is filled with calcium chloride, and the other with soda-lime. *h* contains a little water to indicate the rate of the flow of gas through the apparatus. The rubber connection between *h* and *g* is provided with a Mohr pinchcock, and is closed, whenever practicable, to prevent the absorption of moisture by the soda-lime in the outer limb of *g*.

The calcium chloride in the tubes *a*, *b*, and *d* must, of course, be free from calcium oxide or other alkaline substances. Solutions of the fused commercial salt, however, always exhibit a strongly alkaline reaction. Material suitable for this experiment may be prepared by adding ammonium chloride to a solution of commercial calcium chloride, evaporating, and heating until the ammonium salt has been expelled.

Weigh about half a gram of pulverized and dried Iceland spar or other pure carbonate into the flask 1 and add to it a little water. Weigh the absorption tubes *e* and *f*. Connect the different parts of the apparatus, tying with shoemaker's waxed thread all joints made with rubber tubing. Close the stopcock in the dropping funnel. Open the pinchcock between *g* and *h*, and attach *h* to a filter pump. If the apparatus is tight, the air will soon cease to bubble through the water in *h*. Fill the dropping funnel with dilute hydrochloric acid, allow a little of it to flow into the flask below, and disconnect from the filter pump. Introduce other small quantities of acid from time to time until the mineral is dissolved. Remove with a pipette the greater portion of the acid remaining in the funnel. Connect the funnel with the Geissler bulbs, and aspirate air through the apparatus at a moderate rate, heating the flask meanwhile nearly to the boiling point. Avoid all active ebullition in order to prevent, as far as possible, the distillation of water into the U-tube nearest the flask. Continue to draw air through the apparatus until the weighed tubes, which become hot during the absorption of carbonic acid, have been quite cold for a period of five or ten minutes. Remove and weigh the tubes *e* and *f*.

For a second determination it is necessary only to refill *a* and *e*, and to exchange the places of *e* and *f*.

The method is an excellent one and is applicable to all carbonates.

II. THE VOLUMETRIC DETERMINATION OF CARBONIC ACID

Weigh into a beaker about 0.2 gram of ground and dried Iceland spar, add a little water, and measure in about twice the quantity of standard hydrochloric acid, which is required to dissolve the mineral. Cover the beaker with a watch glass. When the material is dissolved, rinse the under side of the covering glass back into the beaker, add a little methyl orange,

and neutralize with a very dilute water solution of potassium hydroxide whose concentration need not be known. Having found the volume of the alkali required to neutralize the excess of hydrochloric acid, measure off an equal portion of the alkali and titrate it with the standard hydrochloric acid, using methyl orange as the indicator. The difference between the volume of the acid added to the calcite and that required to neutralize the alkali is the volume of hydrochloric acid required to decompose the carbonate. If the standard acid is very dilute, e.g. one-tenth normal, the solution of the carbonate may be hastened by gently warming the liquid. Its temperature should not, however, be allowed to rise above 50° or 60° .

This method is applicable to all substances containing carbonates, provided they do not at the same time contain oxides or salts (decomposed by hydrochloric acid) whose acids are not sensitive to methyl orange, — such salts, for example, as borates, sulphides, and certain silicates.

There are many other methods of determining carbonic acid in carbonates. All of them may, however, be arranged in one or another of the three following groups.

1. The carbonate is heated with a weighed quantity of some nonvolatile substance which at high temperatures displaces the carbonic acid, — such substances, for example, as borax glass, sodium metaphosphate, silica, and potassium bichromate. The acid in some carbonates may, of course, be expelled by heat alone.

2. The carbonate is decomposed in a weighed vessel by an acid, but under such conditions that only the dried carbonic acid can escape. In this, as in the preceding case, the carbonic acid is determined by loss.

3. The gas derived from the carbonate by decomposing it with an acid is collected and measured. A great variety of forms of apparatus have been devised and recommended for methods 2 and 3.

THE SEPARATION OF CARBONIC FROM OTHER ACIDS

The substances whose presence is likely to give rise to difficulties when carbonic acid is determined by the method employed in Exercise XXXVII are peroxides, fluorides, sulphides, sulphites, and thiosulphates.

1. Peroxides decompose hydrochloric acid with evolution of chlorine. Hence, if these are present in the material under examination, some other acid (nitric or sulphuric) should be used to liberate the carbonic acid. If the material also contains chlorides, the carbonic acid gas must be made to pass through a solution of silver sulphate before entering the absorption apparatus.

2. If fluorides, excepting calcium fluorides, are present, the carbonate should be decomposed with tartaric or citric acid.

3. Hydrogen sulphide is readily absorbed by pumice stone containing anhydrous copper sulphate. Hence no danger is to be apprehended from the presence of a sulphide in the carbonate unless the conditions are such as to give rise to the formation of sulphur dioxide. In that case the sulphur must be oxidized to sulphuric acid by the addition of neutral potassium chromate.

4. Sulphites and thiosulphates also are to be converted into sulphates by potassium chromate before liberating the carbonic acid. But in such cases sulphuric or nitric acid should be employed rather than hydrochloric acid; and if chlorides are present, the gas must be purified by passing it through a solution of silver sulphate.

FILTRATION IN AN ATMOSPHERE FREE FROM CARBONIC ACID

When solutions of the caustic alkalies and alkaline earths are filtered, the carbonic acid of the air must be excluded. Figure 53, 1, 2, and 3, represents convenient and simple forms of apparatus for such exclusion. They may also be employed for filtration in an atmosphere of nitrogen or of hydrogen. Tubes

filled with solid potassium hydroxide are attached by means of rubber tubing to *a*, *b*, *c*, and *d*, and each connection is provided with a Mohr pinchcock. The parts marked *e* contain the filters. If asbestos is to be used, the forms of *e* represented in 1 and 3 are employed. If, on the other hand, a paper filter will suffice, the form of *e* represented in 2 is to be used. In 1, *e* consists of the simplest form of calcium chloride tube. The filter is made in the same manner as a Gooch filter, upon a perforated porcelain disk placed in the bottom. In 2, *e* consists of two funnels, one inverted over the other, whose edges are held together by a rubber band. In 3 two large cylindrical funnels, such as are employed when filtering with a Gooch crucible, are

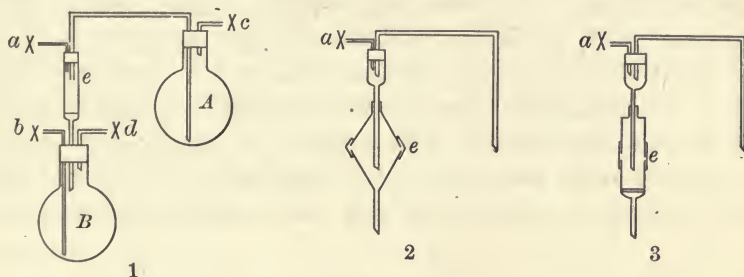


FIG. 53

used. Their edges are also held together by a rubber band. The filter is made in the same manner as for *e* in 1. The flask *A* contains the liquid to be filtered and *B* receives the filtrate. These flasks are not represented in 2 and 3. Ordinarily a bottle rather than a flask is employed to receive the filtered liquid.

The filter pump is attached to the potassium hydroxide tube at *d* and the pinchcock at *a* is opened. After a time *a* is closed and *b* is opened. Finally, the pump is attached to *c* and *a* is opened. Having thus freed the whole apparatus from carbonic acid, the pump is attached to *d* and *c* is opened. Having in this way filled the funnel with the liquid to be filtered, *c* is closed and *a* is opened. To refill the funnel at any time it is necessary only to close *a* and open *c*.

If it is desired to filter in an atmosphere of nitrogen, the potassium hydroxide tubes at *a*, *b*, *c*, and *d* are exchanged for absorption apparatuses containing an alkaline solution of pyrogallous acid.

To filter in an atmosphere of hydrogen, the stoppers in *A* and *e* are supplied with small vent tubes, drawn out to fine points, which may be opened and closed; *d* is drawn out to a fine point and bent downward to a right angle to dip under mercury; while *a* and *c* are connected each to a limb of a Y-tube. The hydrogen is generated in a Kipp's apparatus, and enters the filtering apparatus—properly purified and under pressure—through the third limb of the Y-tube. The remaining steps are as follows: (1) *a* and *b* are opened; (2) *b* is closed and *d* is opened; (3) *d* is closed and the vent in *A* is opened; (4) *a* is closed and *c* is opened; (5) the vent in *A* is closed and that in *e* is opened, filling the funnel; (6) *c* and the vent in *e* are closed and *a* is opened. The pressure of the hydrogen upon the liquid in the funnel forces the latter through the filter. To refill the funnel, *c* and the vent in *e* are opened and *a* is closed.

DETERMINATION OF CARBONIC ACID IN THE AIR

There are three principal methods of determining atmospheric carbonic acid, each of which has been variously modified in respect to details.

1. A large measured volume of air is slowly aspirated through weighed absorption tubes. The arrangement usually employed for this purpose is that proposed by Brunner, which permits a simultaneous determination of atmospheric moisture. It consists of a large gasometer of ascertained capacity, which is filled with water and serves as an aspirator, and a series of six connected U-tubes, which for convenience will be designated by the letters *a*, *b*, *c*, *d*, *e*, and *f*. The tube *a* is connected with the aspirator, and the others follow in alphabetical order. The tubes *a*, *b*, *c*, and *f* are filled with small pieces of pumice

stone which have been moistened with concentrated sulphuric acid, while the intermediate pair, consisting of *c* and *d*, contain moistened calcium hydroxide. All the tubes except *a* are weighed. The air is deprived of its water while passing through *f* and *e*, and of its carbonic acid while passing through *d* and *c*. The tube *b* retains any water which may have been acquired by the dry air while passing through *d* and *c*. The increase in the weight of the three tubes *b*, *c*, and *d* gives the carbonic acid contained in the volume of air which was aspirated through the apparatus, while the increase in the weight of *e* and *f* gives the amount of water in the same.

Some of the details requiring special attention are the following: (1) Owing to the permeability of rubber to moisture and carbonic acid, the glass tube ends should be brought close together within the rubber connectors, and the latter should be painted externally with shellac for some distance on either side of the glass joint; (2) the pumice stone must be freed from chlorine; for this purpose it is thoroughly moistened with concentrated sulphuric acid and then heated to redness in a Hessian crucible.

Since the quantity of carbonic acid contained in the air is very minute (under normal conditions only about 3 volumes in 10,000, or 0.03 of 1 per cent), the amount of air which must be drawn through the apparatus is usually very great. If the air is not more than ordinarily rich in carbonic acid, 100 liters of the former will yield about 30 cc. of the latter, and the increase in the weight of the absorption tubes *b*, *c*, and *d* will be about 60 milligrams.

The weight of water obtained from a given volume of air is, as a rule, about eight times as great as that of the carbonic acid. It is to be remarked that if air is dried to the fullest possible extent by concentrated sulphuric acid, and is afterwards passed through weighed tubes containing phosphorus pentoxide, an increase in the weight of the latter is observed, showing that sulphuric acid is an imperfect dehydrating agent for gases.

2. The carbonic acid in a known volume of air is absorbed by a measured quantity of a standard solution of barium hydroxide, and the excess of the alkali is determined by means of a standard solution of oxalic acid. This is Pettenkofer's method.

If the air to be examined is rich in carbonic acid, the determination is made in the following manner: A glass-stoppered flask having a capacity of about 6 liters is carefully calibrated and filled with the air under investigation. Forty-five cubic centimeters of the standard solution of barium hydroxide are introduced and the flask is closed. From time to time, for an interval of half an hour, the flask is rotated in such a manner as to spread the solution over the glass surface within. Afterwards the liquid is quickly poured into a glass cylinder and covered to protect it from the carbonic acid of the air. Finally, when the precipitate of barium carbonate has subsided, a measured portion of the clear solution is withdrawn by means of a pipette and titrated with the standard acid.

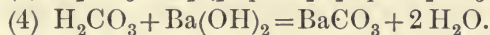
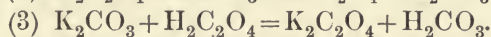
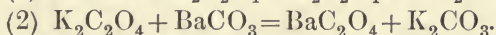
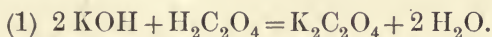
If the air does not contain more than the normal proportion of carbonic acid (approximately 3 parts in 10,000), a much larger volume of it should be treated. It is then advisable to employ some efficient form of gas-absorption apparatus for the standard barium hydroxide, and a large aspirator of known capacity. Having removed the carbonic acid from a sufficiently large quantity of air, the contents of the absorption tubes must be transferred to a graduated vessel in which they may be diluted to a known volume. This is made necessary by the evaporation which occurs while the air is being aspirated through the standard solution.

A method proposed by Mohr differs from that of Pettenkofer in that the barium which is precipitated as carbonate is determined instead of the unneutralized hydroxide. For this purpose the solution of hydroxide, after absorption of the carbonic acid, is filtered and washed, and the carbonate remaining on the filter is dissolved in hydrochloric acid. The barium may then be weighed as chloride after evaporation of the solution, or as sulphate after precipitation by sulphuric acid.

One source of error in the method of Mohr has been found in the fact that a paper through which the hydroxide has been filtered retains barium even though the filter was washed with water until the filtrate gave no reaction for the metal. The magnitude of the error and therefore the amount of the correction to be applied may be ascertained by filtering a solution of equal concentration through a paper of the same size as that to be used in the experiment, afterwards extracting with hydrochloric acid, and determining the weight of the barium which has been retained.

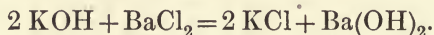
A somewhat similar difficulty has been observed in the case of all methods which involve the use of a standard solution of barium hydroxide. In contact with glass a portion of the metal is rendered insoluble and the concentration of the solution thereby diminished. Errors from this cause are easily avoided by first washing with portions of a standard solution of barium hydroxide all glass surfaces with which it is to come in contact.

A standard solution of barium hydroxide which is to be used with one of oxalic acid must not contain even traces of the caustic alkalis. The reason for this exclusion will appear if we consider the following equations which represent the reactions which take place when oxalic acid is added to a solution containing a caustic alkali, barium hydroxide, and suspended barium carbonate:



The potassium oxalate and barium carbonate which are formed as represented in equations (3) and (4) again react as indicated in equation (2), etc. The barium carbonate which is necessary for the institution of this recurring series of reactions is never wanting in unfiltered solutions of the hydroxide, and it is

nearly always formed in small quantities during a titration, in consequence of unavoidable exposure of the solution to the air. To ascertain whether a given solution of barium hydroxide contains a caustic alkali, it is necessary only to filter it out of contact with the air, to measure off two equal portions of the filtrate, to add to one of these a small quantity of pure barium carbonate, and finally to titrate both portions with oxalic acid. If the portion to which the carbonate was added requires more acid for its neutralization than the other, a caustic alkali is present. A solution of barium hydroxide containing a caustic alkali may be rendered fit for use with oxalic acid by the addition of barium chloride:



It is hardly necessary to mention the fact that in computing the proportion of carbonic acid, the temperature, pressure, and the hygroscopic condition under which the air was measured must be taken into account.

3. A measured portion of air is deprived first of its moisture, and second of its carbonic acid by absorption, and the contraction which takes place in each operation is determined in a graduated and calibrated apparatus which permits the correct reading of minute differences of volume. The best apparatus yet devised for this method, whether for the determination of carbonic acid or of atmospheric moisture, is that of Pettersson.*

THE PREPARATION OF CARBONIC ACID GAS FREE FROM AIR

The usual methods of preparing carbonic acid gas for laboratory purposes are:

(1) By heating a carbonate — acid sodium carbonate, magnesite, manganese carbonate, or a mixture of sodium carbonate and potassium bichromate — and (2) by decomposing a carbonate with some acid — acid sodium carbonate, marble, or magnesite.

* *Zeitsch. anal. Chem.*, 25, 467.

Both of these methods, as they are ordinarily employed, yield a product which is contaminated with air. The reasons for this are sufficiently obvious. In the first place, it is difficult wholly to displace the air within the vessels in which the carbonic acid is generated. Much may be accomplished, however, by giving to the vessels a rational form, i.e. a form which will facilitate the expulsion of the air by the carbonic acid. In general, it may be said that they should be made as narrow in every part as is practicable, in order that the current of gas moving toward the exit may be as rapid as possible; also that they should have no "dead spaces," i.e. spaces where the gas may come to a partial rest. Moreover, the arrangement of parts should be such that the direction of the current is generally upward rather than downward.

Again, if acids are used to decompose the carbonate, the absorbed air becomes a source of contamination which is usually very persistent. This difficulty may be partially remedied by boiling, provided the acid is a nonvolatile one or does not thereby become too dilute. If the acid cannot be boiled and the absorbed air must be expelled by displacement, a narrow form of generator is especially advantageous.

But the most serious difficulty presents itself when compact minerals, like marble and magnesite, especially the former, are employed as the source of the carbonic acid. These always contain air, which is slowly liberated during the entire time that the mineral is undergoing decomposition either by heat or by an acid. In the case of marble it has been proposed to extract the included air by placing the fragments of the mineral under water, which is afterwards boiled for a long time; also by placing the wet material under the bell of an air pump and exhausting. Neither of these remedies is efficacious though both are of some value. It is better in all cases, if practicable, to reduce the carbonate which is to serve as the source of the gas to a fine powder.

By careful attention to the form of the generating apparatus and its connections, and to the condition of the materials, it is

possible to diminish the proportion of air in the gas to limits which, for most purposes, are tolerable. If a purer gas is required, the following method is recommended.

A hard glass tube somewhat longer than a combustion furnace is closed at one end and nearly filled with finely powdered and dried magnesite. The open end is then drawn out and attached to a Sprengel pump. The tube is exhausted and then heated throughout its whole length until the pressure within is restored. It is then allowed to cool and to remain for some time undisturbed. Afterwards it is again exhausted. The gas which will be obtained on reheating the magnesite will be quite free from air.

If still greater precautions are thought to be necessary, it is well to reheat, cool, and again exhaust the tube.

The determination of carbonic acid in other gas mixtures than air is considered in a later chapter.

CHAPTER XV

THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS

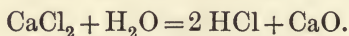
THE DRYING OF GASES

As a rule, the hydrogen and carbon of organic compounds are oxidized, the former to water and the latter to carbon dioxide, and the products of the oxidation are collected in weighed absorption tubes. The absorbents employed for carbon dioxide are either soda-lime or potassium hydroxide, usually the latter. Both are efficient and no extraordinary precautions are necessary in their use. The proper management of the materials employed for the collection of the water—calcium chloride, sulphuric acid, phosphorus pentoxide, etc.—is, on the other hand, a matter of some difficulty and requires a knowledge of the peculiarities of each.

1. CALCIUM CHLORIDE

The salt is used in two forms, as “granular” and as “fused” calcium chloride. The first is obtained by evaporating a solution of the compound to dryness and heating the residue for a long time at about 200° . The product still contains from 20 to 26 per cent of water, or approximately two molecules. The fused material is anhydrous except in so far as it has acquired water in consequence of exposure. The anhydrous or fused form absorbs water with somewhat greater avidity than the granular, though the difference between them in this respect is not great at low temperatures. Solutions of both the fused and the granular salt exhibit an alkaline reaction

owing to the presence of calcium hydroxide derived from the oxide which is formed during the drying of the chloride:



If the chloride is to be used for the determination of water in a gas which also contains carbon dioxide, the presence in it of calcium oxide cannot, of course, be tolerated. It is often attempted to escape the mischievous effect of the presence of the oxide by passing a current of dry carbon dioxide or of dry hydrochloric acid gas through the tube containing the chloride, before using the same for the absorption of water. It has been shown, however, that the conversion of the oxide into carbonate or chloride by this means is only superficial, and that the material is therefore again in condition to absorb carbon dioxide whenever its outer surface is moistened with water.

The granular form may, however, be obtained in a neutral condition, i.e. free from oxide, by evaporating a solution of the chloride with ammonium chloride and heating the residue until the latter salt has been expelled.

Calcium chloride, whether granular or fused, is an imperfect drying agent. This has been repeatedly proved by passing a moist gas through a series of weighed tubes containing the chloride and then through other weighed tubes containing strong sulphuric acid. It has been uniformly found that though the weight of the last calcium chloride tube in the series remained unchanged, the first sulphuric acid tube became heavier. Furthermore it was shown by Dibbits that when saturated air is dried to the fullest possible extent by calcium chloride containing 26.22 per cent of water or 2.19 molecules, the gas still retains per liter the following quantities of water: 0.3, 1.0, or 3.3 milligrams, according as the desiccation is effected at 0°, 15°, or 30°. These quantities correspond respectively to 6, 8, and 11 per cent of the total amount of water originally in the saturated air.

That the efficiency of calcium chloride as a drying agent is greatly modified by temperatures was also shown by Dibbits in the following manner:

Air dried by calcium chloride at the temperature of the room was passed through a number of other weighed calcium chloride tubes. The two end tubes of the series remained at the temperature of the room, while those which intervened were maintained at other temperatures, some above and some below that of the room. The results of an experiment of this kind are given below in tabular form. The letters in the first vertical column, from *a* to *e*, designate the tubes in their order, the dried air entering *a* and then passing through *b*, *c*, etc. The second column gives the temperatures of the various tubes during the passage of the air, and the third their gain or loss in weight.

TEMPERATURE OF THE ROOM 16.9°

TUBES	TEMPERATURE	CHANGE IN WEIGHT
<i>a</i>	16.9°	0.0000 gram
<i>b</i>	0.0°	+ 0.0452 "
<i>c</i>	30.2°	- 0.1565 "
<i>d</i>	0.0°	+ 0.1559 "
<i>e</i>	16.9°	- 0.0442 "
Total		+ 0.0004 "

It appears from the foregoing table that if air which has been dried by calcium chloride at one temperature is passed over another portion of the salt having a different temperature, it (the air) will gain or lose water according as the temperature of the second portion of calcium chloride is higher or lower than that of the material by which it was first dried. Stated in another way, the weight of the individual absorption tubes in a series through which previously dried air is passing may be increased or diminished at will by simply lowering or raising their temperature. If the tubes by which the gas enters and leaves the series have the same temperature as the calcium

chloride by which the air was first dried, the algebraic sum of the gain and loss will be zero within the limits of necessary errors in the weighing of such apparatus.

The important bearing of these facts on the determination of hydrogen in organic compounds, as well as on all other quantitative operations in which water is collected in a similar manner, will appear later.

2. SULPHURIC ACID

As stated already, concentrated sulphuric acid is a better drying agent for gases than calcium chloride. The quantities of water which were found by Dibbits to remain in air after drying with calcium chloride are the quantities which are absorbed by sulphuric acid after the air has been dried to the fullest possible extent by calcium chloride.

Moreover, the efficiency of sulphuric acid is much less influenced by temperature. It desiccates nearly equally well at all temperatures between -30° and $+25^{\circ}$. Above 30° its efficiency declines, but not rapidly.

It has been stated that when a gas containing carbon dioxide is conducted over or through sulphuric acid, a sensible quantity of this constituent is retained by the acid. It appears, however, that all of the carbon dioxide so retained is easily removed by passing through the acid another gas, e.g. air, which is free from the dioxide.

A certain degree of volatility at ordinary temperatures has also been ascribed to the acid, but Morley has shown that a liter of air which has passed through pure sulphuric acid of 1.84 specific gravity, at ordinary temperatures, cannot contain more than from 0.002 to 0.003 milligram of sulphuric anhydride (SO_3). If the presence of pyrosulphuric acid, from which the trioxide does volatilize, is to be apprehended, the acid may be diluted with 6 or 8 per cent of water, which will not materially diminish its efficiency as a desiccating agent.

Sulphuric acid often contains sulphur dioxide, but this may be removed by boiling or by passing air through it.

The best form of absorption tube for sulphuric acid, as well as for most other absorbents, is usually the glass-stoppered U-tube with small side tubes — for the entrance and exit of the gas—which are opened or closed by turning the stoppers. These are filled with fragments of broken glass or with beads, which are then thoroughly moistened with the acid. The quantity of the acid is so regulated that the portion which collects in the bottom shall not quite fill the horizontal part of the tube. The glass can be remoistened at any time by turning the tube first in one direction and then in another.

3. PHOSPHORUS PENTOXIDE

The most energetic of all absorbents for water is phosphoric anhydride. It is, however, but little used except in cases where the extreme desiccation of a gas is necessary. The objection to its more frequent employment is the exceedingly viscous liquid which is formed wherever water comes in contact with the oxide. This liquid soon clogs a tube filled in the ordinary manner and prevents the passage of gas. The difficulty is partially remedied by loosely filling the tube with glass wool and then distributing the pentoxide through it in such a manner that no large quantity of the absorbent is collected in any one place, especially in the end of the tube through which the gas enters. Usually a straight tube only partially filled with the pentoxide is employed. A channel for the passage of the gas can then always be secured by giving to the tube a horizontal position and tapping until the material distributes itself along the bottom. Whenever such a course is practicable, a gas which is to be dried by phosphorus pentoxide should first be made to pass through strong sulphuric acid. It will then enter the pentoxide in a nearly dry condition, and the formation of any considerable quantity of the viscous liquid will be avoided. The

degree of desiccation will be the same, of course, as if the anhydride alone had been used.

Commercial phosphorus pentoxide sometimes contains the trioxide. This may be removed by resublimation in a current of dry air.

If air dried to the fullest possible extent by sulphuric acid is passed through weighed phosphorus pentoxide tubes, the latter increase slightly in weight. The increase is, however, by no means so great as that observed when air dried by calcium chloride is made to pass through sulphuric acid. According to Dibbitts it amounts to about 0.002 milligram per liter of air, and according to Morley* it is precisely this quantity of water which strong sulphuric acid is unable to remove from the air.

The question whether a gas which has been dried by phosphorus pentoxide still contains water has been investigated in a very ingenious manner by Morley. Air dried by phosphorus pentoxide was drawn, with the aid of a vacuum pump, through a glass apparatus consisting of one piece but having in reality two parts. Part I, that first entered by the gas, contained moistened calcium chloride, and Part II, phosphorus pentoxide. The gas, in passing from I to II, was made to traverse an exceedingly fine capillary tube, and it therefore entered the second compartment in a greatly expanded condition. If now the apparatus should be found to lose weight, the loss must be due to the inability of the oxide in II completely to desiccate the air with its diminished tension of water vapor. A minute loss in weight was observed, amounting to about 0.25 milligram of water in 10,000 liters of gas. As estimated by the experimenter, air passing through the apparatus at the rate of three liters per hour would occasion in ten years a loss of weight amounting to about 10 milligrams.

* *Zeitsch. anal. Chem.*, 24, 541.

4. ANHYDROUS COPPER SULPHATE

According to Fresenius, anhydrous copper sulphate is somewhat less hygroscopic than calcium chloride. The method by which it is usually prepared for use in drying a gas is that proposed by Stolba. Fragments of pumice stone are placed in a concentrated solution of copper sulphate and the liquid is boiled until the air has all been expelled from the stone. The pieces are then drained, dried, and heated to the temperature required to dehydrate the sulphate (about 200°).

5. CALCIUM OXIDE

Quicklime, even though freshly heated, is markedly less efficient as a drying agent than any of the substances hitherto mentioned. According to Van der Plaats it leaves twice as much water in a gas as calcium chloride.

6. POTASSIUM HYDROXIDE

Calcium oxide and fused potassium hydroxide are employed to dry ammonia gas. The latter substance is far more efficient for this purpose than the former. As a desiccating agent for gases not containing carbon dioxide it is said to excel calcium chloride (Van der Plaats).

Fresenius arranges the absorbents investigated by him in the following order, according to their efficiency:

1. Quicklime.
2. Anhydrous copper sulphate.
3. Calcium chloride (fused and granular).
4. Concentrated sulphuric acid.
5. Phosphorus pentoxide.

In nearly all quantitative operations in which water is absorbed and weighed dry air or some other gas must be

employed to sweep the water into the absorption apparatus, and it is in drying the air so employed that the most serious mistakes are likely to be made. On the basis of what has already been said regarding the various absorbents, the following rule may be formulated: The same kind of material should be used to dry the air and to absorb the water; in other words, the material employed for the one purpose should be just as efficient as and no more so than that used for the other. Suppose, for example, that an organic compound has been burned by copper oxide in a glass tube in the usual manner, and that the water is to be collected and weighed in a calcium chloride tube; the current of air which is introduced into the combustion tube for the purpose of carrying the water into the absorption apparatus must also be dried by calcium chloride. Moreover, the two drying apparatuses must be maintained at nearly the same temperature. If the air were dried by sulphuric acid and the water absorbed by calcium chloride, the result would be too low; while if the reverse arrangement were adopted, it would be too high.

Rubber stoppers and tubes are always a source of embarrassment in the determination of gas constituents. They are somewhat permeable to water, carbon dioxide, etc., and certain precautions are therefore necessary in their use. A tube which is to be weighed should not be closed with a rubber stopper but rather with a good cork whose projecting end is smoothly covered with sealing wax. It is better, of course, whenever practicable, to use for absorbents tubes which are closed by accurately ground glass stoppers. If the different parts of an absorption apparatus must be joined by means of rubber tubes, the glass ends of the adjacent parts should be brought as close together as possible. The rubber connectors should be tied with shoemaker's waxed thread, and the space between the ties should be painted with shellac. The tubing which is to be used in making such connections should be first dried by placing it, while hot, in a desiccator over strong sulphuric acid, and all pieces of rubber so employed should be kept in the desiccator

when not in use. All rubber connectors should be removed before weighing an absorption apparatus, and the latter, when out of use, should be kept in a desiccator with some of the same material with which it is filled.

In order to avoid any error which might arise in a determination of water from a hydrated condition of the glass, the tube in which the water is to be formed or liberated should be subjected to a preliminary heating, and while hot there should be conducted through it a current of dry air. If practicable, the temperature to which it is raised should be higher than that to which it will be subjected in the actual determination.

The articles relating to the desiccation of gases, which may be read with advantage, are indicated below.*

MATERIALS EMPLOYED IN THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS

1. COPPER OXIDE

The oxide which is sold under the designation "for organic analysis," if it has not been previously used, is generally sufficiently free from objectionable impurities. Such material usually requires only to be heated in an atmosphere of air or oxygen — in order to oxidize any metallic copper or organic matter which it may contain and to expel water — and to be thereafter protected from moisture and dust. A hard glass tube, with an internal diameter of 15 or 16 mm. and somewhat longer than a combustion furnace, is drawn out at one end to permit the attachment of a small rubber tube. A plug of ignited asbestos or a short roll of clean copper wire gauze is placed in the end which was drawn out, and the remainder of the tube is nearly filled with the copper oxide to be heated. The tube,

* Fresenius, *Zeitsch. anal. Chem.*, **4**, 177; Dibbits, *Zeitsch. anal. Chem.*, **15**, 121; Morley, *Zeitsch. anal. Chem.*, **24**, 533; **27**, 1; Van der Plaats, *Recueil des Travaux Chimiques, etc.*, **6**, 45.

with an efficient drying arrangement attached to each end,—calcium chloride or concentrated sulphuric acid,—is placed in a combustion furnace, and the oxide is heated for a long time to low redness in a current of air or of oxygen which is aspirated or forced by pressure through the apparatus. The tube is afterwards very slowly and uniformly cooled and is left with the drying apparatus attached until the oxide is required for use. Since two grades of copper oxide, “coarse” and “fine,” are used in every combustion, it is necessary to prepare a quantity of both kinds; and for this purpose it is more convenient to employ two tubes, each of which contains only one grade of the oxide.

Another method of preparing the oxide, which is often used, is as follows: The oxide is placed in a Hessian crucible, with the addition of a small quantity of nitric acid, if it contains much metallic copper, and is heated in a furnace to redness, but not sufficiently high to cause the formation of a copper silicate. The crucible is removed from the furnace, and the oxide, while still very hot, is transferred to a flask which is afterwards closed with a calcium chloride tube as soon as the temperature of its neck will permit. A pear-shaped flask of uniform thickness is usually employed, and to avoid the danger of cracking, it is heated in a sand bath before introducing the hot oxide. The crucible is grasped with a pair of tongs and the oxide poured into the flask through a copper funnel.

The copper oxide which is used in organic analysis should be free from (1) the alkalis, (2) the alkaline earths, and (3) the chlorides of copper. The first two lose or recover carbon dioxide according to the temperature of the copper oxide, while the chlorides of copper are decomposed by hot moist air with liberation of hydrochloric acid. The presence of the alkalis may be detected by boiling a portion of the oxide in a platinum or porcelain dish with water of neutral reaction, filtering, and treating the filtrate with phenolphthalein or litmus. If an alkali is found, the whole body of the oxide should be boiled with water, filtered, and thoroughly washed with hot water.

Calcium, which is sometimes present in the form of carbonate, may be found by digesting a small quantity of the oxide with warm acetic acid, precipitating the copper by hydrogen sulphide, filtering, and treating the filtrate with ammonium oxalate. To remove the carbonate, the oxide must be digested for a long time with water containing a little nitric acid, filtered, and thoroughly washed. Copper oxide which has been treated for the removal of alkalies or of calcium carbonate must, after drying, be heated by one of the methods previously given, or in a muffle. Copper oxide containing chloride is purified by heating it in a glass tube through which a current of moist air is passing. When the escaping vapors no longer exhibit an acid reaction, a current of dry air is substituted.

2. LEAD CHROMATE

Lead chromate is used instead of copper oxide when the substance to be analyzed contains sulphur, or a halogen, or is difficult to burn. It is prepared in the following manner: A solution of lead acetate ("sugar of lead") is slightly acidified with acetic acid and treated with a small excess of potassium bichromate. The precipitate of lead chromate is collected upon a cotton cloth which is stretched on a wooden frame, and washed with water until the filtrate is found to be free from potassium. The material is then dried, fused in a Hessian crucible, and poured, while in a molten condition, upon a cold stone or iron plate. The cooled mass is broken up — for the most part pulverized — and sifted in order to separate the fine from the coarse material. Finally, the various grades are dried at a temperature somewhat above 100° in flasks or tubes which are afterwards provided with calcium chloride tubes to protect the chromate from the moisture of the air.

A given volume of lead chromate contains one and one-half times as much oxygen as an equal volume of copper oxide. At a red heat it fuses, and at higher temperatures it gives up a

portion of its oxygen. The product of this decomposition is a mixture of chromic oxide and basic lead chromate. When only moderately heated it oxidizes less energetically than copper oxide. Its greater efficiency at higher temperatures is due to its fused condition and to the liberation of oxygen.

It has frequently been noticed that a sample of the chromate which had been prepared for use in organic analysis gave up, on being fused, a quantity of carbon dioxide. It has not, however, been ascertained whether the gas so liberated was absorbed while the chromate was, at some previous time, in the molten condition, or whether it resulted from the oxidation of organic matter with which the material had become contaminated.

Lead chromate may be used for three or four combustions without reoxidation, but if longer service is required of it, it should be moistened with nitric acid, dried, fused, etc. If occasionally treated in this manner, the material may be used indefinitely.

Formerly lead chromate was supposed to be less hygroscopic than copper oxide, and its use was therefore recommended in cases in which an exact determination of hydrogen was required. This opinion appears, however, to have been erroneous.

The rather easy fusibility of lead chromate is an objection to its use except in the case of those substances which are the most difficult to burn. R. de Roode* has overcome this difficulty in a very satisfactory manner by mixing with the powdered chromate one-fourth its weight of red oxide of lead. The mixture is washed in a funnel with water and drawn, with the aid of the filter pump, into a compact mass. While still moist the material is broken up with a spatula into pieces about the size of a pea, which are heated to redness, a small portion at a time, in a porcelain crucible. When cold, the pieces are still further broken up in a porcelain mortar into pieces about the size of wheat grains, and the finer material is separated from the coarser by sifting. This mixture does not liquefy at a red heat.

* *Am. Chem. Jour.*, 12, 226.

3. METALLIC COPPER

When an organic compound containing nitrogen is burned with copper oxide or lead chromate, more or less of the nitrogen is converted into nitric oxide. The formation of this compound takes place even though the nitrogen in the substance burned is not in direct combination with oxygen. The nitric oxide thus formed, if not destroyed, would be converted by oxygen and water into nitric and nitrous acids, and these would be absorbed in the calcium chloride and potassium hydroxide which are employed to collect the water and carbon dioxide. In practice it is always destroyed by reduction to nitrogen, and the reducing agent is always metallic copper. The choice of metals available for this purpose is exceedingly limited, owing to the fact that most of the metals which are capable of depriving nitric oxide of its oxygen also reduce carbon dioxide.

Copper, in contact with moist air, becomes tarnished with oxide, and in this condition it is unfit for the reduction of nitric oxide. It is therefore necessary first to subject the metal itself to the action of some reducing agent in order to give to it a fresh metallic surface. The most effective agent for this purpose is hydrogen, but unfortunately copper, when heated in an atmosphere of hydrogen, occludes a considerable quantity of the gas and does not readily give it up again. The copper may also be, and usually is, reduced by the vapors of some inflammable liquid of low boiling point, like methyl alcohol.

Either of the following methods will yield a product suitable for the reduction of nitric oxide.

1. A hard glass tube is compactly filled with granular copper oxide and heated to dull redness in a combustion furnace. Hydrogen gas — which has been purified by passing through an acid and afterwards an alkaline solution of potassium permanganate — is conducted over the hot oxide. When the reduction is complete, the current of hydrogen is exchanged for one of air,

which is likewise made to pass through the permanganate solutions and also through a calcium chloride tube. The oxygen of the air is absorbed on entering the tube, and a portion of the copper — that nearest the entrance — is converted into oxide. The remainder of the copper is surrounded by an atmosphere of nitrogen, into which the occluded hydrogen diffuses and by which it is carried out of the tube. The temperature of the metallic copper should be raised, while the nitrogen is passing over it, somewhat higher than that to which the oxide was heated while undergoing reduction, and the current should be continued until a layer of oxide 75 or 100 mm. in length has been formed. Afterwards the tube is slowly cooled — first the portion containing the metal and lastly that containing the oxide — and the copper is transferred to a convenient vessel and placed in a calcium chloride desiccator. According to Hempel,* copper prepared in the manner described above contains no hydrogen.

2. Compact rolls of closely woven copper wire gauze — having a diameter slightly less than the internal diameter of the combustion tube in which they are to be used — are dropped, while red hot, into a glass tube 250 mm. in length, in the bottom of which are a few drops of methyl alcohol, and the tube is closed with a cork to prevent reoxidation. When cold the roll is transferred to an air bath and heated for some time at a temperature of 140°. According to G. Neumann,† copper reduced by methyl alcohol yields, when burned in air or oxygen, small quantities of water and carbon dioxide. It has also been proposed by Th. Weyl‡ to prepare metallic copper for organic analysis by passing vapors of formic acid over the hot oxide.

It appears that the hydrogen occluded by copper is capable of reducing carbon dioxide to the monoxide, thereby affecting the determination of carbon as well as that of hydrogen.

* *Zeitsch. anal. Chem.*, 17, 414.

† *Ibid.*, 32, 99.

‡ *Ibid.*, 21, 559.

4. OXYGEN

The oxygen required to complete the combustion of organic compounds is best prepared by heating the usual mixture of finely powdered potassium chlorate (20 parts) and pyrolusite (1 part). The mixture is placed in a glass or metallic retort — having a capacity not less than twice the volume of the powder and provided at its outlet with a rather wide rubber tube to conduct the oxygen into the gasometer — and is heated, gently at first and afterwards more vigorously, with a triple burner which is held in the hand. When the mass begins to melt, the retort is gently shaken in order to effect a uniform distribution of the heat; and when the evolution of gas becomes quite strong, the end of the rubber tube is inserted in the gasometer. The commercial “compressed” oxygen usually contains hydrocarbons and cannot be used in the combustion of organic compounds.

One gram of potassium chlorate yields about 2.7 liters of oxygen. The gas contains chlorine and usually carbon dioxide, both of which, however, are removed while the oxygen is passing through the apparatus described under 5.

5. AN APPARATUS FOR THE PURIFICATION OF OXYGEN AND AIR

The air and oxygen employed in the determination of carbon and hydrogen must, before entering the combustion tube, be freed from water, carbon dioxide, and any other possible constituents which could affect the weight of the absorption apparatus. The arrangement employed to effect this purification consists of (1) a U-tube about 150 mm. in height, which is filled with soda-lime or with small pieces of potassium hydroxide; (2) another U-tube of equal size, which is filled with calcium chloride or with fragments of glass (or pumice stone) moistened with concentrated sulphuric acid. The U-tubes are closed with corks carrying small glass tubes bent to a right angle, and the exposed portions of the cork are covered with sealing wax. In

joining the two, the ends of the small glass tubes are brought close together within a short piece of rubber tube, which is then tied and painted with shellac. When not in use, the entrance and exit ends of the apparatus are closed with rubber tubes and glass plugs. Whether the second U-tube is to contain calcium chloride or sulphuric acid will, of course, depend upon which of these reagents is to be employed for the absorption of water.

6. AN ABSORPTION APPARATUS FOR WATER

Whether calcium chloride or sulphuric acid is used as the absorbent, the best form of U-tube for the collection of the water is that which is opened and closed by means of ground-glass stoppers. If a tube of this kind is not available, the "Marchand" tube or any one of its numerous modifications will answer the purpose. The tube should have a height of 75 or 80 mm., and an internal diameter of 10 or 12 mm. If it is necessary to close it with stoppers, corks and not rubber should be used, and these should be covered with sealing wax.

Calcium chloride, owing to the never-failing presence of the oxide, must be exposed for a long time to an atmosphere of carbon dioxide before employing it for the absorption of water. To this end, the tube — compactly filled with small pieces of the chloride and in other respects ready for use — is attached to another drying tube, which is in turn connected with a carbon dioxide generator. Before weighing the tube the carbon dioxide remaining in it is displaced by air. As previously stated, the oxide in calcium chloride cannot be wholly converted into carbonate by dry carbon dioxide. For this reason the contents of the tube must be frequently renewed and never allowed to become visibly moist. When out of use the tube is to be kept in a desiccator containing calcium chloride.

Pumice stone usually contains chlorides which in contact with sulphuric acid yield hydrochloric acid. Hence, if this material is to be employed for the absorption of water, the

pieces, before filling the tube with them, must be heated for a considerable time with the concentrated acid in order to insure the decomposition of the chlorides and the removal of the volatile hydrochloric acid.

7. AN ABSORPTION APPARATUS FOR CARBON DIOXIDE

This consists, when the water is absorbed by calcium chloride, of two pieces, — a Geissler or Liebig apparatus, preferably the former, for liquid potassium hydroxide, and a U-tube, one limb of which is filled with solid potassium hydroxide, and the other with calcium chloride, the two materials being separated by a thin partition of ignited asbestos which is placed in the middle of the horizontal part of the tube. The solution of potassium hydroxide should have a specific gravity of about 1.35, and the bulbs of the Geissler apparatus should not be more than one-half full. The gas which passes out of the combustion tube is dried by the calcium chloride, and then gives up its carbon dioxide in the Geissler apparatus. But in passing through the solution of potassium hydroxide it acquires a certain quantity of water, — the amount depending, of course, on the temperature and concentration of the solution. It is to deprive the gas of this water, as well as to detain any carbon dioxide which may have escaped absorption in the Geissler apparatus that the U-tube filled with solid absorbents is employed. The limb of the tube which contains the alkali is the one connected with the Geissler bulbs. With this arrangement the waste gas passes last over calcium chloride, and therefore leaves the absorption apparatus for carbon dioxide with the same tension of water vapor as it entered it. There is, of course, a slight positive error due to the change in the volume of the gas while passing through the alkaline solution.

If the water is determined by absorption in sulphuric acid instead of calcium chloride, the arrangement of the apparatus for the collection of carbon dioxide must be somewhat different.

It should then consist of (1) a Geissler apparatus containing a solution of potassium hydroxide, (2) a tube filled with solid potassium hydroxide, and (3) a tube filled with pumice stone or glass beads moistened with sulphuric acid.

8. TUBES FOR PROTECTION AGAINST ATMOSPHERIC WATER AND CARBON DIOXIDE

The contents of the combustion tube and of the various absorption apparatuses must at all times be protected against the carbon dioxide and the water of the air. It is therefore necessary to have at hand a number of tubes filled with absorbents for these compounds, which may be attached wherever their protection is required. Tubes filled half with calcium chloride and half with soda-lime will suffice for the protection of a weighed absorption apparatus containing calcium chloride and also for the protection of the combustion tube, if the water resulting from the combustion is to be collected in calcium chloride. But if an absorption apparatus contains sulphuric acid, the arrangement employed for its protection against the air must also contain this acid. Sulphuric acid should likewise be used to protect the contents of the combustion tube when the water is to be collected in that acid.

EXERCISE XXXVIII

DETERMINATION OF CARBON AND HYDROGEN

I THE COMBUSTION OF A SOLID IN THE OPEN TUBE

(Applicable to compounds not containing nitrogen)

The hard glass tube which is used in this exercise should be about 100 mm. longer than the furnace and should have an internal diameter of 15 or 16 mm. The rough ends are to be softened in the flame to prevent the mutilation of the stoppers, and the interior of the tube is to be thoroughly cleansed and

dried. Each end is provided with a tightly fitting, singly perforated rubber stopper. A short glass tube with a ground-glass stopcock is inserted in one of the stoppers,—that in the end through which oxygen enters the combustion tube. The other stopper, which receives the absorption apparatus for water when the final preparations are made, should *fill* the tube, leaving no space between it and the glass for the lodgment of water.

The manner of filling the tube is indicated in Fig. 54. The space *a* is filled with copper oxide, which is kept in place by the short rolls of oxidized copper wire gauze *b* and *b'*. The portion of this space nearest *b* and *b'* is filled with the coarser oxide, and the remainder with the finer. The space *c* is occupied by another roll of oxidized copper wire gauze having a length of 100 or 120 mm. The space *d* is left vacant for the boat which is to contain the material to be burned. Behind *d*,

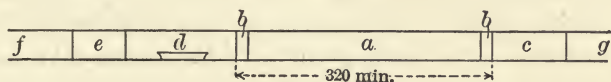


FIG. 54

in *e*, is still another roll of oxidized copper wire gauze 70 or 75 mm. in length, and to this is attached a copper wire extending nearly to the end of the tube. The rolls *b*, *b'*, *c*, and *e* are made, of the proper dimensions, from closely woven wire gauze and oxidized in another tube by conducting over them, while hot, a current of dry air or oxygen.

Having filled the tube in the manner indicated, place it—without the boat—in the combustion furnace, taking care that the trough in which it rests is straight and smoothly lined with asbestos paper. Attach the apparatus for the purification of oxygen and air at *f*, and close the end *g* with a stopper carrying an unweighed calcium chloride tube. Heat the portion within the furnace—slowly and as uniformly as possible—to dull redness, and aspirate through the tube a slow current of air. When it is believed that the contents of the tube have been sufficiently

desiccated, gradually diminish the heat without interrupting the current of air. When the tube is cold replace the calcium chloride tube at *g* with the weighed absorption apparatus consisting of (1) the calcium chloride tube, (2) the Geissler bulbs, (3) the U-tube filled partly with solid potassium hydroxide and partly with calcium chloride, and (4) an unweighed tube containing calcium chloride and soda-lime.

Open the tube at *f*, withdraw the roll of wire gauze, and quickly insert the platinum boat containing a weighed quantity of the purest cane sugar, ranging from 0.250 to 0.300 gram. Replace the roll and the stopper, leaving the combustion tube connected with the apparatus for the purification of oxygen.

Heat the roll at *c* and the adjacent half of the copper oxide to a dull red, and then light the burners under *e*. Admit a slow current of oxygen and proceed to heat the remainder of the oxide, advancing gradually toward the substance in the boat. Regulate the temperature in the vicinity of the boat so as to produce a slow decomposition of the sugar, taking care in the meantime to keep the whole body of copper oxide at a red heat. The rapidity of the decomposition may be judged by the amount of carbon dioxide absorbed in the Geissler bulbs. During the early stages of the combustion, while the sugar is giving off volatile matter, only a very slow current of oxygen is to be admitted to the tube. Later, when the formation of carbon dioxide has nearly ceased, heat the tube in the vicinity of the boat to redness and increase somewhat the flow of oxygen. If, as usually happens, water condenses in the exit end of the combustion tube, warm the part where water is seen by inverting over the projecting end of the tube a semicircular piece of sheet iron which extends for a short distance into the furnace. If necessary, in order to effect the volatilization of the water, the iron covering may in turn be protected by a piece of asbestos paper to prevent loss of heat by radiation. It is hardly safe to heat the tube near the end with a Bunsen burner, owing to the danger of burning the stopper.

When the charred mass remaining in the boat has been completely burned, and the copper reduced from the oxide during the early stages of the combustion has been reoxidized, exchange the current of oxygen for one of air in order to leave the absorption apparatus filled with the latter gas rather than with the former. This precaution is necessary in order to avoid an error in weighing, which otherwise would result from the fact that oxygen is heavier than air.

Disconnect the absorption apparatus, leaving the combustion tube closed with an unweighed calcium chloride tube, and place the various pieces to be weighed — protected by dry rubber tubes and glass plugs — in the balance case. After half an hour remove the rubber tubes and weigh.

If the combustion tube is slowly and uniformly cooled, it is at once ready for a second determination.

The open tube may also be used for the determination of carbon and hydrogen in compounds containing nitrogen. In that case, however, the roll of wire gauze *c* must be unoxidized and must also be protected from oxidation during the combustion. To this end the roll *e* is only partially oxidized before beginning the combustion, and a current of air instead of oxygen is employed. No oxygen in the free state can then reach *c* until the compound has been burned and all of the copper behind it, both that in *e* and that reduced from the oxide, has been oxidized.

II. THE COMBUSTION OF A LIQUID IN THE OPEN TUBE

(Applicable to compounds not containing nitrogen)

Any liquid organic compound which is free from water and contains neither nitrogen nor sulphur nor a halogen may be employed in this experiment. If the available substance is an impure compound or a mixture of uncertain composition, e.g. coal oil, the determination should be duplicated.

Soften a piece of small glass tubing in the flame of a Bunsen burner and draw it out to a fine, nearly capillary tube about 150 mm. long. Break it in the middle and separate one of the smaller tubes from the larger in the flame, leaving enough glass for a small bulb upon the end of the former. Blow at the thicker end a bulb which will hold about half a cubic centimeter.

Weigh the bulb. Through the center of a metallic disk about 100 mm. in diameter drill a small hole — a disk of tin plate, galvanized sheet iron, or of sheet copper will answer the purpose — and place the disk upon a shallow beaker or other vessel containing a quantity of the liquid to be burned. Pass the tube of the bulb through the hole into the liquid below, and alternately heat and cool the bulb until about 0.2 cc. of the liquid have ascended into it. Remove the bulb, cleanse the portion which was immersed, close the open end in the flame, and weigh again.

Reconnect the weighed absorption apparatus and the combustion tube, as in the preceding experiment, and heat the roll of wire gauze *c* and the adjacent half of the copper oxide to redness. Make a file mark on the small tube near the bulb, and place the bulb in a boat with the scratch downward and the tube extending over the edge of the boat. Place the boat in its proper position within the combustion tube, and break the tube in the boat at the file mark by pressing upon it from above with a rod of some kind which is sufficiently long for the purpose. Quickly replace the roll of wire gauze *c* and the stopper, and then conduct the combustion precisely as in the preceding experiment. Somewhat greater caution will be required, however, owing to the greater volatility of the substance.

If a liquid containing nitrogen is to be burned in the open tube, the process is to be modified in the same manner as for a solid containing this element.

III. COMBUSTION IN THE CLOSED TUBE

It is recommended that some solid compound containing nitrogen, but free from sulphur or a halogen, be selected for this experiment.

Figure 55 represents the "bayonet" tube, which is the form usually employed. Its length is to be so regulated that, when finished, each end extends from 50 to 75 mm. beyond the furnace.

After cleansing and drying the tube, place it in the furnace and attach to each end a calcium chloride drying apparatus. Heat the tube to a uniform dull red and aspirate through it a current of air. This treatment of the glass should be continued for an hour or more in order to insure its complete dehydration. Discontinue the current of air and cool the tube very

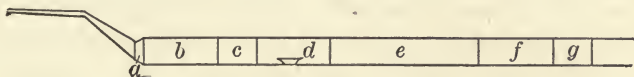


FIG. 55

slowly and uniformly in order to secure a good annealing of the glass. Without removing the drying apparatus fuse off the "bayonet" end of the tube at a point near, but not too near, the rubber which connects it with the calcium chloride tube.

The manner of filling the tube will be indicated by reference to the figure.

a is a short plug of ignited asbestos which prevents the copper oxide from entering the bayonet. To prepare the asbestos for this use, it is heated in a platinum dish over the blast lamp and placed, while still warm, in a desiccator.

b is a layer of coarse copper oxide about 100 mm. in length.

c is a layer of fine copper oxide about 50 mm. in length.

d, a space 100 mm. in length, or longer if the substance is very volatile or the quantity of it is large, is occupied by the substance to be burned and by more of the fine oxide. In filling

the tube the layer *c* is introduced, then the boat containing the compound, and finally as much of the finer oxide as may be thought necessary. By many *b* and *c* are separated by a short plug of asbestos to prevent the finer oxide from sifting into the coarser. This precaution is hardly necessary, however, unless the two grades of oxide differ widely in respect to fineness.

e is a layer of coarse copper oxide about 200 mm. long.

f is a roll of bright copper wire gauze (or a layer of metallic copper reduced from the oxide) 100 mm. or more in length. The purpose of the metallic copper is to reduce oxides of nitrogen; it may, of course, be omitted and the tube made correspondingly shorter when the substance to be burned contains no nitrogen.

g is a layer of coarse copper oxide, or a roll of oxidized wire gauze, about 50 mm. in length, which serves to burn any carbon monoxide formed from the dioxide while passing over the metallic copper. Such reduction of the dioxide is improbable unless the copper contains iron, and the precaution of placing the oxide before the metal is therefore often dispensed with.

The tube should be filled with the least possible exposure of the contents to the moisture of the air. To this end it is well to have all necessary materials at hand before beginning, to open the tube and the flasks containing the copper oxide only when necessary, and to close them as quickly as possible. These precautions are made necessary by the highly hygroscopic character of copper oxide. It is the common experience, however, that the closed-tube method gives somewhat too high percentages of hydrogen in spite of all possible care in manipulation.

Place the filled tube in the furnace, make a file mark across it close to the small end of the bayonet, and attach the weighed absorption apparatus. Draw a little air out of the apparatus by suction and then allow it to reënter slowly. The solution of potassium hydroxide in the Geissler bulbs will rise into the upper bulb of the part nearest the combustion tube, and if the

joints are all perfect, the level of the liquid will thereafter remain unchanged. If the liquid gradually descends, the leaky connection must be sought out and made tight.

Heat *g*, the right-hand half of *e*, and a little of each end of *f* to redness. Afterwards heat the portion of *b* nearest *a* and the remainder of *f* also to redness. Having thus provided for the combustion of any moderate quantity of volatile matter and the reduction of oxides of nitrogen, gradually heat the remaining copper oxide, advancing from both directions towards the substance, and so regulating the temperature in its vicinity as to produce a slow combustion.

Insert the apparatus for the purification of oxygen and air between the bayonet and the gasometer, and admit enough oxygen to produce a slight overpressure. When the solution of potassium hydroxide rises in the Geissler bulbs in the direction of the combustion tube, break off the end of the bayonet, admitting the oxygen, and heat the copper oxide in the vicinity of the boat to redness. As soon as the copper reduced from the oxide appears to be reoxidized, and before the roll of wire gauze is attacked, exchange the current of oxygen for one of air and allow *f* to cool. The remaining steps are the same as in the preceding experiments.

The procedure is not materially changed for the combustion of a liquid. The substance is introduced into the tube in a bulb, as in experiment II, and the stem is broken off in the same manner at a file mark made near the bulb. The heating of the tube requires, of course, somewhat greater care than when a solid is burned.

IV. THE COMBUSTION OF A COMPOUND CONTAINING SULPHUR

The compound selected for this experiment may also contain nitrogen and it may be burned in the open or in the closed tube. The necessary modifications of previous procedure are given on page 364.

a. Combustion in the Open Tube

The tube is filled as directed under I, Exercise XXVIII, except in the following particulars: (1) the space *a* is filled with lead chromate prepared by de Roode's method, instead of with copper oxide; (2) if the compound to be burned contains nitrogen, the roll *c* is to be substituted by one of unoxidized copper wire gauze, and the roll *e* is to be oxidized only partially.

The burning of the compound is conducted as directed under I, except in the case of nitrogenous substances, which are better burned in a current of air than in one of oxygen.

b. Combustion in the Closed Tube

The tube is filled as directed under III, except that lead chromate is used throughout in place of copper oxide, and the process of burning is the same as when the closed-tube method is employed for compounds which are free from sulphur.

V. THE COMBUSTION OF A COMPOUND CONTAINING A HALOGEN

When an organic compound containing a halogen is burned with copper oxide, a cuprous salt is formed which at a red heat volatilizes and is decomposed by free oxygen into copper oxide and the halogen.

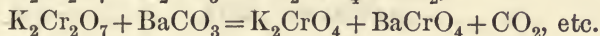
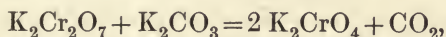
There are various ways of obviating this difficulty, of which the following are the best:

1. The substance is burned with lead chromate, in which case a lead salt of the halogen is formed. The open or the closed tube may be used. It is well, however, in either case to heat the chromate near the exit end of the tube only moderately. If the substance contains nitrogen also, the roll of copper wire gauze or a layer of the metal reduced from the oxide must be placed in the tube in the usual position.

2. The substance is burned in the ordinary manner, with copper oxide either in the open or in the closed tube, but a roll

of bright silver foil 150 mm. in length is placed in the exit end of the tube and moderately heated during the combustion. If the substance contains nitrogen, a roll of copper wire gauze must also be used.

When organic compounds containing metals of the alkalis or of the alkaline earths are burned, stable carbonates are formed; it is therefore necessary in such cases to add to the oxidizing material some substance which is capable of decomposing carbonates. These compounds are usually burned with a mixture of lead chromate (10 parts) and of potassium dichromate (1 part). The results are then normal; for, at a red heat,



The methods employed in the preceding exercise provide only for the determination of the carbon and hydrogen of organic compounds. There are other methods, not so much used, which accomplish a simultaneous determination of carbon, hydrogen, and nitrogen, and still others which enable one to determine the oxygen in organic compounds. Respecting these, as well as some other methods which differ essentially from those already employed, the student is recommended to consult the following sources:

Fresenius, *Quant. Analyse*, 2, 97-110.

Wheeler, *Jour. prak. Chem.*, 96, 239.

Zeitsch. anal. Chem., 5, 217.

Schulze, *Zeitsch. anal. Chem.*, 5, 269.

Frerichs, *Ber. d. d. chem. Ges.*, 10, 26.

Kopfer, *Zeitsch. anal. Chem.*, 17, 1.

Hempel, *Zeitsch. anal. Chem.*, 17, 409.

CHAPTER XVI

THE DETERMINATION OF CARBON IN IRON AND STEEL. THE INCINERATION OF ORGANIC SUBSTANCES. THE DETER- MINATION OF ORGANIC MATTER IN WATER

EXERCISE XXXIX

DETERMINATION OF TOTAL CARBON IN IRON AND STEEL

I. BY DIRECT COMBUSTION IN A CURRENT OF OXYGEN

There are required for this experiment:

1. About 3 grams of steel filings or fine turnings free from grease and other impurities.
2. A glazed porcelain tube having an internal diameter of 16 or 18 mm. The required length of the tube depends upon the length of the furnace in which it is to be used. A short furnace with 12 or 15 burners will suffice, and it is necessary only that the tube shall be from 150 to 200 mm. longer than the furnace. A short roll of oxidized copper wire gauze is placed in the tube near the middle; and one of the two spaces into which the tube is thus divided is completely filled with granular copper oxide to a point which, during the combustion, will lie near the end of the furnace. Another roll of oxidized wire gauze is then inserted to keep the oxide in place. There is also prepared a third roll of oxidized wire gauze 100 mm. in length, to which is attached a copper wire with a loop on the end. This, as is customary in all similar combustions, is placed

in the rear end of the tube after the insertion of the boat containing the material to be burned. Each end of the porcelain tube is provided with a rubber stopper through which is passed a small glass tube. For the better protection of the stoppers against radiated heat, the glass tubes are made to project a few millimeters into the porcelain tube, and over the projecting ends are placed perforated disks cut from thin asbestos board. Any organic matter which these disks may contain is destroyed by heating them for a time to redness in a platinum dish.

3. A supply of oxygen in a gasometer, and the usual apparatus for the purification of that gas.

4. An apparatus to be attached to the exit end of the porcelain tube for the absorption of water and sulphur dioxide. This consists of a U-shaped tube, the vertical limbs of which are filled with calcium chloride, and the horizontal portion with lead superoxide, the two reagents being separated by asbestos or cotton wool.

5. An absorption apparatus for carbon dioxide which, as in the combustion of organic compounds, consists of (1) a Geissler apparatus containing a solution of potassium hydroxide (sp. gr. 1.35), and (2) a U-tube filled partly with solid potassium hydroxide and partly with calcium chloride, the two absorbents being separated by asbestos.

6. A tube filled partly with calcium chloride and partly with soda-lime to protect 5 from the carbon dioxide and the moisture of the air.

Heat the porcelain tube, with 4 in place, to redness — raising the temperature very gradually — and pass dry oxygen through it. Cool it slowly, and when cold attach 5. Test the apparatus for leaks and then heat to redness the portion of the tube which contains the copper oxide. Spread the weighed steel filings evenly over the bottom of a capacious porcelain boat. Insert the boat and the roll of oxidized wire gauze, and conduct the combustion as directed in Exercise XXXVIII under VI. The tube should be maintained at a red heat for nearly an hour before exchanging the current of oxygen for one of air.

This method is applicable to the determination of total carbon in all forms of iron. It is necessary, however, that the material be quite finely divided, since otherwise a portion of the carbon may escape oxidation.

The total carbon in iron, like carbon in organic compounds, may also be determined by combustion in the closed glass tube. The essential features of the procedure are given below.

1. The material in a finely divided condition is mixed in a porcelain mortar with 15 parts by weight of powdered lead chromate and 1.5 parts of potassium chlorate or the same weight of potassium bichromate. A little ignited asbestos is placed in the bayonet end of the glass tube, and upon this a layer of powdered lead chromate, 25 mm. in length. The mixture containing the iron is then introduced through a funnel, and thereafter several small portions of the lead chromate which have been previously used to rinse the mortar. The filled tube is held in a horizontal position and gently tapped to produce a channel for the passage of gas. If potassium chlorate has been mixed with the iron, the tube which is attached to the exit end of the combustion tube for the absorption of water must contain a quantity of anhydrous copper sulphate as well as calcium chloride. The combustion is carried out in the usual manner.

2. The filings or powdered material are mixed in a mortar with 20 or more parts by weight of fine copper oxide. The tube is filled in the same manner as in 1 except that copper oxide is used throughout in the place of lead chromate. For the absorption of water and sulphur dioxide, the apparatus described under 4 in the preceding exercise is employed. The combustion is conducted in a current of oxygen.

II. BY OXIDATION WITH CHROMIC ACID

There are required :

1. A flask having a capacity of 300 cc. This is provided with a doubly perforated rubber stopper. Through one of the

holes is passed a short glass tube bent to a right angle, and through the other a separating funnel with a glass stopcock. The funnel should have a capacity of not less than 100 cc., and the orifice at the delivering end should be small. The right-angled tube serves for the exit of the gas, and the separating funnel for the introduction of the reagents.

2. An apparatus for the purification of air. This consists of a U-tube filled with soda-lime or with pieces of solid potassium hydroxide. It is connected with the upper end of the separating funnel by means of a tube bent to two right angles.

3. A series of three connected U-tubes in which the carbon dioxide is dried before entering the weighed absorption apparatus. The first, that nearest the flask 1, is empty, while the second and third are filled with calcium chloride.

4. The usual apparatus for the absorption of carbon dioxide, together with the tube for the protection of its contents from the carbon dioxide and the moisture of the air.

Weigh about one gram of pig-iron drillings into the flask. Connect the different parts of the apparatus and test the whole for leaks. Introduce into the flask through the funnel from 10 to 15 cc. of a saturated solution of chromic acid, and then very cautiously 100 cc. of concentrated sulphuric acid which has been heated to the boiling point with a little chromic acid, and afterwards, when cold, allowed to stand over crystals of chromic acid until saturated. Introduce also in the same manner 50 cc. of dilute sulphuric acid having a specific gravity of 1.10. Heat the flask gradually nearly to the boiling point of the solution. When the evolution of gas ceases, conduct two or three liters of air through the apparatus, slowly lowering the temperature of the flask meanwhile.

The foregoing processes 1 and 2 provide for the determination of total carbon in iron and steel without previous removal of the iron in the sample. There are also various methods by which the iron may be separated from the carbon in such a manner as to leave the whole of the latter in the form of an

insoluble residue. The carbon in such residues is not pure, and it is therefore necessary to burn them and to collect the resulting carbon dioxide in a weighed absorption apparatus. The following are some of the methods by which the separation of iron and carbon is effected.

1. The material is treated with a saturated solution of the double chloride of copper and ammonium, and a quantity of concentrated hydrochloric acid, and afterwards stirred until the precipitated copper is redissolved. The residue of carbon is collected upon an asbestos filter, — preferably upon one which has been made in a platinum boat with a perforated bottom, — washed, dried, and burned. Instead of the ammonium salt the double chloride of copper and potassium may be employed to dissolve the iron.

2. The sample, in a single piece if practicable, is placed in a basket of closely woven platinum wire, which is suspended in a beaker and connected with the positive pole of a single Bunsen or Grove element. In the same beaker, but connected with the other pole of the battery, is a piece of platinum foil. The beaker is filled to the requisite depth with a solution of 1 part by volume of concentrated hydrochloric acid in 4 parts of water, and the current is so controlled by the introduction of resistance that no gas escapes from the iron. The residue of carbon, which usually retains the form of the sample, is transferred to an asbestos filter, washed, dried, and finally burned.

3. The material, in a porcelain boat, is placed in a glass tube and heated in a current of chlorine until all of the iron has been volatilized in the form of ferric chloride. The residue contains the carbon, also any slag and manganese which may have been in the sample. It is transferred to an asbestos filter, washed, to free it from nonvolatile chlorides, dried, and burned.

III. BY OXIDATION OF THE CARBON AFTER REMOVAL
OF THE IRON

Treat about one gram of pig-iron drillings in a beaker with 100 cc. of a saturated solution of copper-ammonium chloride and 7.5 cc. of strong hydrochloric acid. Stir the solution vigorously for some minutes and then place the beaker in a warmed bath but not where its temperature can rise above 60°. Continue to stir at frequent intervals until the precipitated copper is dissolved. Allow the undissolved material to subside and then filter through ignited asbestos.

A suitable filter may be made in the following manner: A perforated platinum or porcelain disk is placed in the bottom of a cylindrical glass funnel like that used with the Gooch crucible, and upon it is made, in the usual manner, a filter of asbestos which has been previously ignited.

Wash the precipitate and dry it at 100°. Transfer it, together with the filter, to a platinum or porcelain boat. Wipe out the funnel with ignited asbestos, and add the material so employed to the boat. Burn the carbon as directed under I, having previously placed a roll of silver foil in the exit end of the porcelain combustion tube.

Repeat the determination, oxidizing the carbon with chromic acid. The apparatus required for this purpose is the same as that described under II except as regards the arrangement for the purification of the carbon dioxide. This consists of (1) a Peligot tube containing a solution of silver sulphate in concentrated sulphuric acid; (2) an empty U-tube; (3) a U-tube filled with pumice stone which has been saturated with a concentrated solution of copper sulphate and subsequently heated to dehydrate the salt; (4) a tube filled with granular calcium chloride. The apparatus for the absorption of carbon dioxide is the same as that usually employed.

Transfer to the flask the asbestos filter on which the material to be burned has been collected and washed, and also the asbestos

used in cleaning the funnel. Add through the separating funnel 10 cc. of a saturated water solution of chromic acid and then 100 cc. of concentrated sulphuric acid which has been heated nearly to the boiling point with a little chromic acid. Pass a slow current of air through the apparatus, and very gradually raise the temperature of the liquid in the flask nearly to the boiling point. When the oxidation is complete slowly cool the flask, continuing for a time the current of air.

EXERCISE XL

DETERMINATION OF GRAPHITIC CARBON IN IRON

Treat 1 gram of pig-iron drillings with 15 cc. of nitric acid of 1.2 specific gravity. Collect the undissolved material upon an asbestos filter and wash it thoroughly with hot water. Treat the residue on the filter with a hot solution of potassium hydroxide of 1.1 specific gravity. Wash thoroughly with water, afterwards with dilute hydrochloric acid, and finally with water. After drying, burn the carbon by either of the methods previously used.

Repeat the determination, proceeding in the following manner: Treat 1 gram of the iron with an excess of hydrochloric acid of 1.1 specific gravity. When the solution of the iron is complete, boil for a few minutes and then allow the graphite to subside. Decant through an asbestos filter. Wash by decantation several times, using hot water. Treat the residue with 30 cc. of a solution of potassium hydroxide of 1.1 specific gravity, and when effervescence ceases, heat the solution to the boiling point. Collect the graphite upon the asbestos filter and wash first with water and finally with alcohol and ether. Burn the carbon in the same manner as before.

EXERCISE XLI

DETERMINATION OF COMBINED CARBON IN STEEL

COLORIMETRIC METHOD OF EGGERTZ

This method depends upon the fact that when samples of similar varieties of steel or of iron are dissolved in nitric acid of 1.2 specific gravity, the depth of the brown color which is developed in the several solutions is proportional to the quantity of the chemically combined carbon in the samples. It is therefore practicable to determine the combined carbon in any specimen of steel by comparing the color developed on dissolving a known weight of it in nitric acid with the color in a standard solution which has been made by dissolving a weighed quantity of a similar steel whose percentage of carbon is known. If the darker of the two solutions — the solution of the standard and that of the sample to be analyzed — is diluted until both exhibit the same shade of color, equal volumes of them will contain the same quantity of carbon, and the total quantities of carbon in them will be related as the volumes of the solutions.

The percentage of carbon in the steel which is to serve as the standard must be determined by combustion by one of the methods already given. For this particular experiment it is recommended that the steel employed in Exercise XXXIX, 1, be selected for the standard, and that two or three other steels of the same general character and the same history as regards previous treatment be chosen as the material for analysis. Owing to the well-established fact that the condition of chemically combined carbon in steel may be decidedly modified by mechanical means, such as rolling, hammering, tempering, etc., it is quite essential that only those steels which have received the same treatment shall be compared with each other.

Arrange in a rack a series of clean, dry, and numbered test tubes having a length of 150 mm. and a diameter of 15 or 16 mm. Weigh into one of the tubes about 0.2 gram of the standard

steel and into the others nearly equal quantities of the samples to be tested. Place the rack in a bath of cold water and add to each test tube from a graduated pipette the required amount of nitric acid of 1.2 specific gravity, — i.e. for steels containing less than 0.3 per cent of carbon, 3 cc.; from 0.3 to 0.5 per cent, 4 cc.; from 0.5 to 0.8 per cent, 5 cc.; from 0.8 to 1.0 per cent, 6 cc.; over 1.0 per cent, 7 cc. If the percentage of carbon in the samples is not even approximately known, begin by adding 3 cc. of the acid to each, and afterwards increase the quantity, 1 cc. at a time, as the depth of color and the presence of undissolved carbonaceous matter in the solution indicate the need of more acid. The nitric acid must be wholly free from chlorine. Place a small funnel in the mouth of each test tube. Heat the water in the bath to the boiling point and maintain it at that temperature — shaking the tube from time to time — until all of the carbonaceous matter is dissolved. Remove each tube to a bath of cold water as soon as the solution in it becomes clear, taking care to exclude any strong light and especially direct sunlight.

Transfer the various solutions, together with the water used in rinsing the test tubes, to Eggertz graduated tubes. These are clear and colorless glass tubes of uniform caliber, which have been graduated from the bottom upwards for a capacity of thirty or more cubic centimeters.

Dilute the solution of lightest color to about twice the volume of the acid which was used in making it, and then dilute all the other solutions to the shade presented by the first after its dilution. In comparing shades the solutions are, of course, viewed transversely and not in a vertical direction, and the comparison is usually facilitated by placing the tubes containing the solutions to be compared in a rack with a white background.

If the quantity of carbon known to be in the weighed sample of the standard steel is divided by the volume of the standard solution in cubic centimeters, the quotient will be the

quantity of carbon represented by one cubic centimeter of that or of any other solution of the series. Hence, to find the weight of carbon in any one of the samples under examination, it is necessary only to multiply the volume of its solution by this quotient.

Permanent color standards are also employed in the determination of carbon in steel. These are made by dissolving in water certain definite quantities of hydrochloric acid and of the chlorides of iron, copper, and cobalt.

EXERCISE XLII

DETERMINATION OF THE FUEL VALUE OF COAL

The exact analysis of coals and the precise estimation of their value as fuel are problems of considerable complexity, and they cannot therefore be considered in this place. There are, however, certain expeditious processes which, though no high degree of exactness can be claimed for them, nevertheless enable one to ascertain the general character of coals and to determine approximately their relative value for heating purposes. The method here presented is of this kind. It provides for the determination of (1) the water, (2) the volatile combustible matter, (3) the fixed or nonvolatile carbon, and (4) the sum of the inorganic or ash-forming constituents.

Great care must be exercised in securing a sample which shall fairly represent the average composition of the whole supply from which it is drawn. To this end, a shovelful of coal is taken from many parts of the stock. The small portions thus withdrawn are thoroughly mixed in one heap, which is afterwards divided into two equal parts. One of the halves is again mixed and divided as before. The process of mixing and halving is continued until the material has been reduced to a manageable quantity, when the larger pieces are broken into smaller ones. The process of mixing and halving is then resumed;

but after each partition the portion selected for further manipulation is reduced to a still finer condition. Finally, when the material has in this manner been reduced to a volume of about 250 cc., it is transferred to a clean, dry bottle, which is tightly closed to protect the contents from the air and to prevent loss of water by evaporation.

I. DETERMINATION OF WATER

Weigh from 1 to 2 grams of the powdered coal in a weighing glass with a ground-glass stopper and heat in an air bath at a temperature of 105° for exactly one hour. Allow the tube to cool in a calcium chloride desiccator and weigh again. The loss in weight represents the water mechanically inclosed in the coal, but does not include that which is in chemical combination.

II. DETERMINATION OF THE VOLATILE COMBUSTIBLE MATTER

Weigh a fresh quantity of the coal, ranging from 1 to 2 grams, into a platinum crucible. Cover the crucible and heat exactly $3\frac{1}{2}$ minutes over a Bunsen burner, and then, without giving the material time to cool, for the same length of time to the highest temperature attainable over the blast lamp. Place the crucible, while still warm, in a calcium chloride desiccator. When weighed it should be inclosed in a weighing glass with a ground-glass stopper.

The difference between the losses (expressed in percentages) of the first and second experiments is regarded as the percentage of volatile combustible matter in the coal. Since the coal may contain substances having water in chemical combination, which is lost at the temperature of the blast flame but not below 105° , and since it may also contain carbonates which are decomposed at a high temperature, it will be seen that the determination of the volatile combustible matter by this method is somewhat uncertain.

III. DETERMINATION OF FIXED CARBON

Place the crucible on its side in a triangle and burn out the carbon, taking care not to subject the contents of the crucible to unnecessarily strong draughts. The combustion of the carbon may be considerably hastened by stirring the material occasionally with a platinum spatula or wire. The loss in weight is equal to the fixed carbon. The residue of noncombustible matter is the ash, and the sum of the ash and of the fixed carbon is the coke which the coal will yield.

INCINERATION

Incineration is the name given to the process of destroying by combustion in air the organic matter in vegetable and animal substances, with a view to the determination of their inorganic constituents which remain after such treatment, as an "ash." The usual procedure is as follows: The material — freed from extraneous matter and dried under such conditions as may be prescribed by the nature of the investigation — is burned in a roomy platinum dish in a muffle. However simple the process may appear, it is beset with many difficulties, some of which will be mentioned together with the customary methods of meeting them. The ash constituents are often so light as to be carried out of the dish by air currents; hence it is necessary to regulate carefully the draught through the muffle. Again, the combustion must be effected at the lowest possible temperature. This precaution is necessary for several reasons: (1) If any of the constituents of the ash are fused, the unburned carbon becomes incrustated with liquid, which prevents or greatly retards its oxidation. The particular substances which most frequently give rise to this difficulty are the salts of the alkalis, and it is often necessary in the case of materials rich in these compounds to extract the partially burned matter with water before the incineration can be completed. (2) At a full red

heat the alkalis are somewhat volatile. (3) When heated to the point of fusion the meta- and pyro-phosphates decompose the chlorides and sulphates ; hence the volatile constituents of the latter salts may be lost. Some substances, while undergoing the charring process which precedes the actual combustion, "froth" in such a way as to overflow the dish. Materials behaving in this manner must be treated in small portions and with great caution as regards the regulation of the temperature while the frothing continues.

In the case of substances difficult to incinerate, Rose recommends the mixing of the charred material with a weighed quantity of platinum sponge. The coal obtained by the preliminary heating of the substance is transferred to a porcelain mortar and cautiously ground to a fine powder. It is then intimately mixed with 30 grams of the sponge per 100 grams of the original material. The mixture is placed, a small portion at a time, in a large platinum dish and very gradually heated over a Bunsen burner to a dark red. Before the temperature of the mass has risen to that of a visible red, the particles of carbon at the surface begin to burn and the black mixture becomes coated with a gray film. The combustion is hastened by constantly but carefully stirring with a platinum spatula. The glimmering of the mass continues, as fresh portions of it are brought to the surface, as long as any of the carbon remains unburned.

Others have proposed to use barium carbonate, barium superoxide, ferric oxide, etc., instead of the platinum sponge recommended by Rose.

Notwithstanding the most painstaking incineration of organic substances, a portion of the chlorine, sulphur, and phosphorus which they contain may be lost by volatilization. The acid vapors generated during the charring process may decompose the chlorides with formation of hydrochloric acid, while sulphur and phosphorus, in so far as they are constituents of organic compounds, may escape in an unoxidized or only partially oxidized condition. The loss of chlorine and other halogens may

be prevented and the loss of sulphur and phosphorus may be diminished by the addition of strongly basic compounds, such as sodium carbonate, barium hydroxide, calcium oxide, etc. Since, however, the use of such substances embarrasses the determination of other ash constituents, the chlorine, sulphur, and phosphorus are usually estimated in separate portions of the material and by special methods.

If chlorine is to be determined, about 10 grams of the substance, e.g. vegetable matter, is cut or crushed until it is reduced to a sufficiently fine condition and then moistened with a solution containing about one gram of sodium carbonate. The liquid is evaporated and the residues incinerated at the lowest practicable temperature. When the burning of the carbon can no longer be discerned, the soluble matter is extracted with water and the insoluble portion again incinerated.

For the determination of sulphur — also of phosphorus — the material in a state of fine subdivision is treated with very concentrated nitric acid and the liquid is evaporated to dryness on a water bath. The residue is moistened with the acid and the evaporation is continued, but not to dryness. Water is added and then 2 or 3 grams of pure anhydrous sodium carbonate. The mass is again dried on the water bath, stirred with water to the consistency of a thin porridge, and thoroughly mixed with from 20 to 25 grams of pulverized sodium carbonate. The mixture is dried, ground to a fine powder, and heated over an alcohol lamp — but not to the point of fusion — in a silver or platinum dish until it becomes perfectly white. If, on continued heating, the mass fails to lose its color, it is ground, mixed with a little potassium nitrate, and again heated as before. In this manner the sulphur in the material is converted into sulphates and the phosphorus into phosphates. This method is known as that of Knop and Arendt.

DETERMINATION OF ORGANIC MATTER IN WATER

The presence in waters of appreciable quantities of organic matter of vegetable or animal origin is regarded as an element of the highest importance in determining their fitness for domestic uses. But since it is in general wholly impracticable to isolate, or even to identify, the individual organic compounds in any specimen of well or spring water, indirect methods are resorted to which have for their object the testing of the probability and approximately the extent of such contamination.

One of these methods, the "Albuminoid Ammonia Process" of Wanklyn, Chapman, and Smith, has already been presented in the chapter on the determination of nitrogen. The application of it to the question in hand depends upon the fact that most nitrogenous organic compounds of animal and vegetable origin are decomposed by potassium permanganate in the presence of an alkali in such a manner that the nitrogen is to a large extent converted into ammonia. The same nitrogenous compounds yield ammonia and nitrous and nitric acids when decomposed by fermentative processes; hence the presence of the latter substances in a water is regarded as an evidence of previous contamination, and the quantity of them is regarded as an approximate measure of pollution. In a similar manner great weight is attached to the presence of unusual quantities of chlorine in a water, because sodium chloride is an abundant constituent of urine and of other forms of animal waste which are likely to find their way into the water courses both above and below the surface of the ground.

There are numerous processes for the approximate estimation of organic matter in water, which depend upon the fact that the organic compounds always present in polluted waters readily reduce potassium permanganate. Such methods are expeditious, but they cannot afford very precise information as to the total quantity of the contaminating matter, since different compounds are oxidized to different degrees by potassium permanganate, and

since the extent to which any given compound will be oxidized will depend very much upon the length of time allowed for the reaction and also upon the temperature of the water. Some of the processes involving the use of potassium permanganate are given here.

THE METHOD OF KUBEL

One hundred cubic centimeters of the water to be tested are treated in a 300-cc. flask with 5 cc. of dilute sulphuric acid (1 part of strong acid to 3 parts of water), and with enough of a standard solution of potassium permanganate (equivalent to $\frac{1}{100}$ normal oxalic acid) to produce a deep red color. The solution is boiled for 10 minutes and then treated with 10 cc. of $\frac{1}{100}$ normal oxalic acid. The solution, which becomes colorless on the addition of the oxalic acid, is titrated to a faint red color with the standard permanganate. The difference between the total quantity of permanganate used and 10, the volume of the oxalic acid which was added, is the volume of the permanganate reduced by the organic matter in 100 cc. of the water. It is customary to state the results in milligrams of oxygen consumed by 100 cc., i.e. in parts per 100,000.

If nitrites are present, a portion of the oxygen is employed in converting them into nitrates; but the presence of nitrites is in itself a certain evidence of contamination.

THE METHOD OF SCHULZE

One hundred cubic centimeters of the water are treated with 0.5 cc. of caustic soda (1 part of the hydroxide to 2 parts of water), and with 10 cc. — or 15 in the case of very impure water — of a standard potassium permanganate (equivalent to $\frac{1}{100}$ normal oxalic acid). The water is boiled for about 10 minutes, allowed to cool to 60° or even 50°, and treated with 5 cc. of dilute sulphuric acid and 10 cc. of $\frac{1}{100}$ normal oxalic acid. The excess of oxalic acid is then determined by the standard permanganate, as in the method of Kubel, and the result is stated in the same manner.

THE METHOD OF TIDY

This process differs from both of the preceding ones in that the action of the permanganate on the organic matter is allowed to take place at the ordinary temperatures, and also in the manner of determining the excess of the permanganate. A measured quantity of the water (250 cc.) is treated with dilute sulphuric acid (10 cc.) and a definite volume (10 cc.) of a dilute standard solution of permanganate. After standing for 3 hours at the temperature of the room, a small quantity of a solution of potassium iodide is added to the water, and the iodine which is liberated is determined by means of a standard solution of sodium thiosulphate.

In connection with the permanganate processes should be mentioned the method of Fleck, who estimates the organic matter in polluted water by means of its reducing action upon an alkaline silver solution. To prepare the standard silver solution, 17 grams of silver nitrate are dissolved in a little water. This solution is then added to another containing 50 grams of sodium thiosulphate and 48 grams of sodium hydroxide. The mixed solution is boiled for 10 or 15 minutes, to destroy any organic matter in the water, and allowed to settle. To determine its strength, a measured quantity of the liquid is titrated with a $\frac{1}{20}$ normal solution of potassium iodide until a drop taken out with a glass rod and placed upon a white porcelain surface gives a blue color with a drop of a chromic acid and starch solution. The last reagent is prepared by mixing equal volumes of a clear starch solution, a solution of potassium bichromate (1 : 20), and concentrated hydrochloric acid.

The determination is made in the following manner : 100 cc. of the water under examination are treated with 10 cc. of the standard silver solution and boiled for about 10 minutes, or until the precipitate which is at first finely divided becomes more compact and exhibits a tendency towards rapid subsidence. When cold the excess of the silver, i.e. that which remains in

solution, is determined by means of the standard potassium iodide solution, with use of the solution of starch and chromic acid as the indicator. The result is stated in milligrams of silver reduced by the organic matter in 100 cc. of water, i.e. in parts per 100,000.

There are also several methods by means of which may be made in impure waters a more or less accurate quantitative estimation of the organic carbon or of the organic carbon and nitrogen. The failure of all of them to give entirely accurate results is due to the fact that a portion of the organic matter in polluted waters is lost by volatilization during the evaporation which necessarily precedes the combustion of the carbon compounds. A brief summary of the best of the methods of this class is here given.

THE METHOD OF WOLFF, DEGENER, AND HERGFELD

In a retort over the free flame 500 or 1000 cc. of the water are evaporated to about one-half the original volume. During the distillation the retort is connected with a condenser and a receiver. The distillate is examined by one of the permanganate methods for an approximate estimation of the volatile organic matter. The liquid remaining in the retort is transferred to a platinum or glass dish and further evaporated upon a water bath to a volume of about 15 cc. The concentrated liquid is then transferred to a 250- or 300-cc. flask. The retort and also the dish in which the water was last evaporated are washed with a small quantity (10 cc.) of dilute sulphuric acid, and the washings are poured into the flask. The carbon dioxide liberated by the sulphuric acid is removed by warming the liquid to about 50° and by conducting a current of air through the flask. The flask is provided with a stopper carrying a tube bent to an obtuse angle for the exit of the carbon dioxide, a small separating funnel for the introduction of sulphuric acid and air, and a thermometer. The exit tube is

connected with an apparatus for the purification and absorption of the carbon dioxide. This consists (1) of a condenser inclined in an upward direction from the flask, (2) a U-tube filled with calcium chloride for the absorption of water, (3) a U-tube containing coarsely powdered antimony for the absorption of chlorine, (4) another U-tube filled with calcium chloride, (5) the usual weighed absorption apparatus for carbon dioxide, together with a tube containing calcium chloride and soda-lime for its protection against the water and carbonic acid of the air.

To the contents of the flask are added 10 grams of finely powdered potassium bichromate. There are then introduced through the separating funnel 50 or 60 cc. of sulphuric acid, — 3 volumes of the concentrated acid diluted with 2 volumes of water. For a half hour the temperature of the liquid in the flask is maintained at 50° or 55°. During the second half hour it is gradually raised to the boiling point. After boiling for about 10 minutes, air freed from carbon dioxide is aspirated through the apparatus.

THE METHOD OF DUPRÉ AND HAKE

A convenient quantity of the water is acidified with phosphoric acid to decompose carbonates, and evaporated to dryness. The residue is transferred to a platinum boat and burned in a current of oxygen in a glass tube which is properly filled for the combustion of organic compounds containing nitrogen. The carbon dioxide developed during the combustion is collected in a solution of barium hydroxide. The barium carbonate is collected on a filter, washed, and dissolved in dilute hydrochloric acid. The barium in the filtrate is determined as sulphate in the usual manner.

The same authors have also proposed a nephelometric method for the determination of minute quantities of carbon in water. It depends upon the fact that the turbidity produced by the

precipitation of a small quantity of lead carbonate from a dilute solution of lead acetate may, with the aid of suitable standards, be utilized for the estimation of the carbonic acid.

THE METHOD OF DITTMAR AND ROBINSON

1. *Determination of Organic Carbon*

A suitable quantity of the water is treated with $\frac{1}{1000}$ of its volume of a saturated solution of sulphurous acid to decompose any carbonates which may be present, and evaporated to a small volume in a flask of the Erlenmeyer form, and afterwards to dryness in a glass dish. The residue is transferred to a platinum boat and burned with the aid of a current of air in a combustion tube which is filled with copper oxide, etc., in the usual manner. The apparatus for the purification of the carbon dioxide, previous to absorption, differs from the one ordinarily used in that a tube containing a solution of chromic acid in 60 per cent sulphuric acid is inserted between the combustion and the calcium chloride tubes for the purpose of intercepting sulphur dioxide.

2. *Determination of Organic Nitrogen*

Half a liter of water is evaporated to a small volume in a flask which is connected with a condenser and receiver. The ammonia in the distillate is determined colorimetrically. To the liquid remaining in the flask are added sulphurous acid and ferric chloride to destroy nitrates. The solution is gently heated, then treated with a little sodium sulphite, to neutralize any sulphuric acid which may have been formed, transferred to a glass or platinum dish, and evaporated to dryness upon a water bath. The nitrogen in the residue is converted by the method of Varrentrapp and Will into ammonia, which is determined colorimetrically.

THE METHOD OF FRANKLAND AND ARMSTRONG

Determination of Organic Carbon and Nitrogen

As regards the estimation of the characteristic constituents of the organic compounds in impure waters, this process is probably more exact than any of those hitherto mentioned. But since it fails to account for the carbon and nitrogen which are lost during evaporation, it is not an entirely accurate method. It is very complicated ; hence only the outlines of the process can be given here.

The water is treated with sulphurous acid and a small quantity of ferric chloride, to eliminate carbonic, nitric, and nitrous acids, and evaporated to dryness in a bath of special construction. The residue is mixed with copper oxide and transferred to a combustion tube. More of the oxide and also a quantity of metallic copper are introduced. The tube is drawn out, attached to a Sprengel pump, and exhausted. The substance is burned, and the gaseous products of the combustion are collected over mercury and determined by gasometric methods. The substances to be estimated are carbon dioxide, nitrogen, and usually a small quantity of nitric oxide. From the total quantity of nitrogen found must be deducted that which was derived from ammonia and ammonium salts ; and to ascertain the magnitude of this correction, a determination of ammonia in another portion of the water must be made.

CHAPTER XVII

GAS ANALYSIS

The room in which gas-analytical operations are performed should be so located that an even temperature can be maintained for a considerable length of time. It should also have a mercury-tight floor. If this is not practicable, the floor under the work table and for some distance around it should be covered with a single piece of linoleum, the edges of which are raised to prevent the escape of mercury.

The table should have a mercury-tight top and a raised border, and should be level. At one corner, or some other convenient place, it is to be provided with a hole for the escape of mercury into a receptacle placed beneath. The vessel used to receive the mercury which is spilled from time to time upon the table should be covered to protect the contents from the dust of the air, and should be provided with a filter through which the metal must pass before entering it. Fastened to the table top, near one end, is a wooden standard a little more than a meter in height. This is provided with a movable wooden arm having a set-screw by which the arm may be firmly fixed in any desired position. The purpose of the arm is to hold the eudiometer in place during an explosion of its contents. A cork, with one end hollowed out to fit the closed end of the tube, is placed between the wooden arm and the eudiometer whenever an explosion is to be made.

The wooden mercury trough with sides of plate glass, which is usually employed in gas analysis, is shown in Fig. 56. It rests upon a board, at one end of which are two standards surmounted by an inclined grooved piece which is lined with felt and serves as a rest for the eudiometer. Before using the

trough the interior is moistened with a solution of mercuric chloride, and then rubbed till dry with mercury. This treatment causes the mercury to adhere to the wood and thus pre-

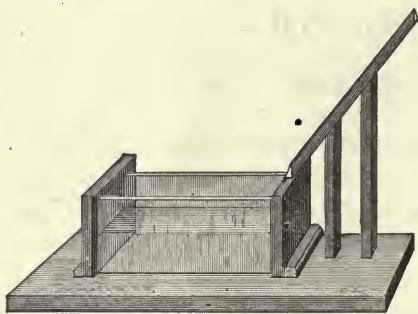


FIG. 56

vents the lodgment of air between them. A rest for the eudiometer, when an explosion is to be made, is prepared by shaping one end of a cork to fit the bottom of the trough and covering the other end with a piece of sheet rubber, which is stretched over the top and tacked to the sides with

steel brads. The rubber covering of the cork, like the bottom of the trough, is rubbed with mercuric chloride and mercury.

There are also required in a room devoted to the analysis of gases:

1. A telescope for reading the eudiometer at a distance.
2. An induction coil with wires running to the work table.
3. A battery consisting of four bichromate cells, or three storage cells, with wires running to the induction coil.
4. A barometer — usually of the siphon variety — which is located so as to be read by the telescope without moving the standard of the latter from its proper position for reading the eudiometer. In the open end of the barometer is placed a cork, with vertically grooved sides, which carries a loosely fitting thermometer. Some time before reading the barometer the mercury in it is set in motion by lowering and raising the thermometer through the cork.
5. Two plumb lines to aid in bringing the eudiometer into a vertical position. These are suspended from the ceiling near the middle of adjacent sides of the room.
6. A Bunsen apparatus for the generation of electrolytic gas, Fig. 57. The inner vessel contains dilute sulphuric acid (1 part

of the concentrated acid to 10 parts of water), while the outer one is filled with water (or, if there is danger of freezing, with alcohol) to prevent the heating of the wires by the current. The enlargements in the upper part of the exit tube are made to hold a small quantity of concentrated sulphuric acid when it is desired to introduce the electrolytic gas into the eudiometer in a dry condition. Before using the gas it must, of course, be allowed to waste until the air has been expelled from the acid and the exit tube.

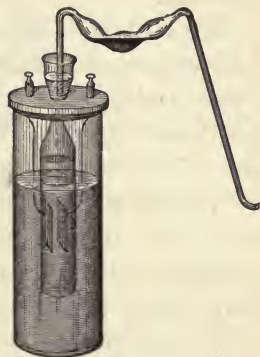


FIG. 57

7. A Bunsen apparatus for the generation of pure hydrogen, Fig. 58. In this the positive pole is located in the bottom of the inner cylinder, where the platinum wire, after passing through the glass, is submerged in mercury in which a little pure zinc is dissolved from time to time. The oxygen which appears at this pole is disposed of in the following manner:

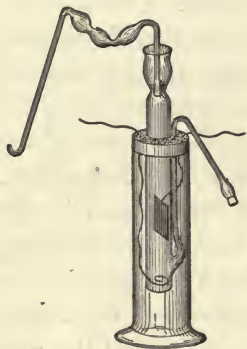
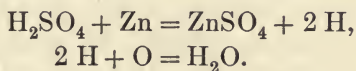


FIG. 58

The zinc in the amalgam is scarcely attacked by the dilute sulphuric acid except while the circuit is closed. The liquid immediately above the positive pole soon becomes saturated with zinc sulphate, which prevents the free diffusion of fresh acid to the zinc amalgam; for this reason the side tube represented in the figure is added to the apparatus. After each experiment the exit tube for gas is removed and fresh acid is poured in at the top, while the concentrated solution of zinc sulphate in the bottom of the cylinder is allowed to escape through the side tube. The acid employed for the generation of pure

hydrogen, like that used in making electrolytic gas, is prepared by diluting 1 part of concentrated sulphuric acid with 10 parts of water.

The calibration of the eudiometer which is to be used in the following experiments, and also the reduction of the volumes of gases which are measured in it, have been fully explained in a previous chapter. The eudiometer should have a length of about 760 mm., though shorter or longer ones may be used.

When a eudiometer is to be filled, previous to the collection of a gas in it, it is well to lay the tube in an inclined wooden trough which is lined with felt, and to introduce the mercury very slowly through a glass tube which reaches to the bottom of the eudiometer. Otherwise air may become entangled between the mercury and the glass, and to remove this often causes much trouble. A good arrangement for filling with mercury is made by attaching the long tube which enters the eudiometer to the stem of a separating funnel with a stopcock, the stem of the funnel having been bent to the proper angle.

The eudiometer having been filled and inverted with its open end dipping under the mercury in the trough, it may be fixed in a vertical position or laid in the inclined grooved piece for the introduction of gas. In ascending, small portions of the gas sometimes become lodged on the side of the eudiometer. To remove these, the tube is tilted to one side or laid in the receptacle at the end of the trough, and by raising and lowering it the mercury column is made to ascend and descend, but in such a manner that the upward movements are more rapid than those in the downward direction. Having introduced the gas, the eudiometer is brought to a vertical position with the aid of the plumb lines, and fastened in the clamp of an iron stand. The operator should then set the mercury in the barometer in motion and retire to a distance until the gas in the tube has had time to take on the temperature of the room, which it will do all the more quickly if he has taken the precaution to use cold gloves or cloths in handling the eudiometer.

The readings to be made are :

1. The height of the barometer and its temperature.
2. The volume of the gas.
3. The height of the column of mercury in the eudiometer above the level of the mercury in the trough.
4. The temperature as indicated by a thermometer whose bulb is buried in the mercury near the lower end of the eudiometer.

It is often necessary in gas analysis to mix gases in eudiometers in certain definite proportions ; in other words, having collected and measured one gas, to introduce another until the volume of the second, if both were measured under standard pressure, bears a predetermined ratio to the volume of the first. But, since the first gas and the mixture are measured under different pressures, the volume of the first, as read upon the millimeter scale, gives no very obvious clue as to when the introduction of the second is to be discontinued. It has been customary, in accordance with the recommendation of Bunsen, to prepare a table for each eudiometer which should show in a general way by actual trial how much space equal volumes of gas will occupy in different parts of the tube, and from which the data required in any given case could be approximately obtained by a process of interpolation.

The difficulty is obviated by considering how the tensions of the two gases, i.e. that of the first and of the mixture made by adding a definite amount of a second gas, are related to each other.

Let v = the volume of the first gas as measured in scale divisions.

t = its tension, i.e. the difference between the height of the barometer and the height of the mercury in the eudiometer.

t_1 = the tension of the mixed gases, i.e. the difference between the height of the barometer and the height of the mercury in the eudiometer after the introduction of the second gas.

v_1 = the volume of the mixed gases as measured in scale divisions.

Then $v_1 = v + t_1 - t$. (1)

Let K = the quantity of the mixture as a multiple of the quantity of the first gas, e.g. if the tube contains air and H_2 is to be introduced, then K will be 1.5, 2, 2.5, or 3, according as the quantity of H_2 is to be 0.5, 1, 1.5, or 2 times as great as that of the air.

Then $K = \frac{v_1 t_1}{vt}$.

Clearing of fractions,

$$Kvt = v_1 t_1. \quad (2)$$

Multiplying equation (1) by t_1 , we have

$$v_1 t_1 = t_1 (v + t_1 - t), \quad (3)$$

and substituting Kvt for $v_1 t_1$ in (3), we have

$$Kvt = t_1 (v + t_1 - t). \quad (4)$$

Finding the value of t_1 in (4), we have

$$t_1 = \frac{-(v - t) + \sqrt{(v - t)^2 + 4 Kvt}}{2},$$

and the height of the barometer, less t_1 , equals the height of the mercury in the eudiometer after the introduction of the second gas, i.e. to what point on the scale the mercury will be depressed.

By assigning the proper fractional values to K , one can determine with equal facility where the mercury meniscus will stand if definite portions of a gas are removed from a eudiometer, e.g. if 0.25, 0.50, or 0.75 of the gas is to be withdrawn, the value of K will be 0.75, 0.5, or 0.25.

EXERCISE XLIII

DETERMINATION OF OXYGEN IN THE AIR

I. BY EXPLOSION WITH HYDROGEN

When a mixture of oxygen and hydrogen is exploded in the presence of nitrogen, as in the determination of oxygen in the air, the proportion of the explosive gases (the oxygen plus twice its volume of hydrogen) to the nonexplosive gases (the

nitrogen plus the excess of hydrogen) must not exceed the ratio of 64 to 100. Otherwise there is danger that a portion of the oxygen will combine with the nitrogen. On the other hand, the proportion of the explosive gases to the nonexplosive must not fall below the ratio of 26 to 100, since, in that case, not all of the oxygen will combine with hydrogen.

It often happens, in introducing hydrogen for the purpose of removing oxygen, that too large a quantity of the gas is allowed to enter the tube, and no explosion, or only a weak one, follows the passage of the spark. In such cases it is necessary to increase the proportion of explosive gases by introducing electrolytic gas, care being taken, of course, not to exceed the limit already given. The volume of the electrolytic gas so introduced need not be measured, since it all disappears on explosion.

Place a minute drop of water in the closed end of the eudiometer, or moisten the inner wall near the top with a damp cloth on the end of a rod. Rest the tube in the inclined rack previously mentioned, fill with mercury, and transfer it to the trough. The air which is to be analyzed must be freed from carbon dioxide, since, if the latter gas is present at the time of the explosion, it will be reduced to carbon monoxide by the excess of hydrogen. For the collection of the air and its introduction into the eudiometer, bulbs with two short and rather narrow stems on opposite sides are to be recommended. These can be readily made by blowing bulbs in the middle of glass tubes and cutting off the ends. They need not have a capacity of more than 15 or 20 cc., even when the determination is to be duplicated. One end is joined by a short piece of rubber to a narrow tube which has been bent to a shape convenient for the introduction of the gas into the eudiometer, while the other end is connected by a rubber tube of some length to a second bulb of the same kind which serves as a reservoir. The bulb which is to hold the air is filled with mercury, and a tube containing a little sodium hydroxide and a small quantity of calcium chloride to absorb carbon dioxide and ammonia is attached to the

exit, and the reservoir slowly lowered. The absorption tube is detached and the air introduced into the eudiometer by raising the reservoir. The amount to be introduced must be determined by the judgment of the experimenter. When the eudiometer is in an upright position, the air will, of course, be much expanded (especially if the tube is a long one), and the quantity of it will seem to be more than it really is.

Having introduced the air, fix the eudiometer in a vertical position with the aid of the plumb lines, set the mercury in the barometer in motion, and retire until the gas has had ample time to take on the temperature of the room. Read with the telescope the volume of the gas, the height of the column in the tube from the level of the mercury in the trough to the top of the meniscus, and the height of the barometer and of the thermometers.

Introduce, without moving the eudiometer, a quantity of hydrogen equal to that of the air, using the formula given on a previous page to determine how far the mercury column will be depressed when, as in this case, K equals 2. Tilt the eudiometer to one side and mix the gases thoroughly by quickly raising and lowering the tube in such a way as to set the mercury column in motion. Restore the eudiometer to its vertical position, allow the mixed gases to cool, and then make the same readings as before. Rest the eudiometer upon the rubber-covered cork, place the cork with one concave end upon the top, and bring the wooden arm down upon it with just enough pressure to hold the tube firmly in place. Explode, remove the corks, and after the contents of the eudiometer have cooled, read again. The percentage by volume of the oxygen in the air is about 20.9.

If the explosion is a weak one, there is a chance that the proportion of explosive gases was too small, and a quantity of the electrolytic gas must be introduced, the contents of the tube well mixed, and the explosion repeated.

When the quantity of the oxygen in a gas mixture is not even approximately known, one begins by adding an amount of

hydrogen so large as to remove all danger of combination of oxygen with nitrogen or of shattering the tube. If then, as usually happens, no explosion or only a feeble one is observed, the proportion of explosive gases is increased by the addition of electrolytic gas until the volume of the gas in the eudiometer is found to remain constant after successive explosions.

The volume of the water which is formed may be neglected in ordinary eudiometric experiments, since it amounts only to 0.00092 of the volume of the gases (under standard conditions) which disappear during the explosion.

II. BY ABSORPTION WITH PHOSPHORUS

Under ordinary pressure pure oxygen is not absorbed by phosphorus. If, however, the oxygen is diluted with another gas, or if the pressure is reduced to about three-fourths of an atmosphere or less, absorption takes place. The reaction is prevented by the presence of various substances. Among these are certain hydrocarbons (such as ethylene), ammonia, and the vapors of ethereal oils and of alcohol. It is also prevented, or very much retarded, by low temperatures. For all gas analytical purposes a temperature not much below 20° should be maintained during the absorption. The formation of ozone may, in certain instances, render impracticable the use of phosphorus as an absorbent of oxygen. This is the case when a gas contains easily oxidized constituents. During the absorption the phosphorus is always surrounded by white clouds, but the absence of these must not be regarded as evidence that oxygen is not present, unless the gas is known to be free from all substances which interfere with absorption.

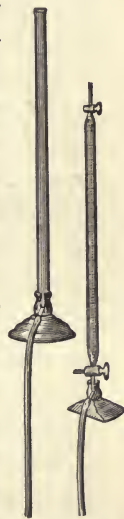


FIG. 59^a

The determination is best made with a Hempel gas burette and absorption pipette, Figs. 59^a and 59^b. The cylindrical bulb

of the pipette is filled with slender sticks of phosphorus. These are prepared by melting phosphorus under water and drawing the liquefied material into a narrow glass tube, which is then dipped in cold water. On solidifying, the phosphorus contracts and slips out of the tube. The pipette is filled with water until the phosphorus is completely submerged and the liquid rises in the ascending limb of the small tube at the side. It is well to protect the phosphorus from the light by covering the bulb containing it with blackened paper.

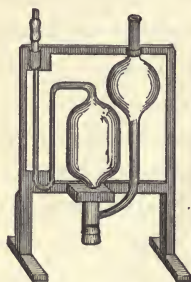


FIG. 59b

The pipette and burette are joined by means of a short piece of glass tubing of very small caliber which is bent to two right angles, and two rubber connectors, as shown in Fig. 60, in which a so-called "simple" pipette for liquid reagents only is exhibited. The manipulation is as follows: The open end of the rubber tube upon the burette, i.e. the portion above the pinchcock, is filled with water, and the glass connecting tube is inserted and crowded down as far as the pinchcock will permit. The glass tube fills with water. The rubber tube upon the pipette is then pinched between the thumb and forefinger to expel the air, and the other end of the glass tube is inserted.

Fill the burette with water and then with air by raising and afterwards lowering the reservoir. See that the water in the graduated and ungraduated tubes has the same level, and then close the burette. Connect the burette and pipette as directed above and slowly force the air from the former into the latter. After a few minutes return the gas to the burette and measure

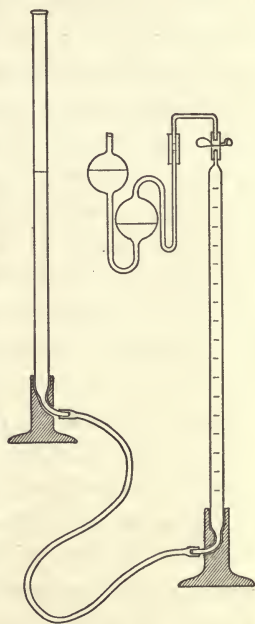


FIG. 60

it. Return it to the pipette and then to the burette, and measure again. If the readings are identical, the absorption is complete. If they are not, the gas must be again exposed to the phosphorus. As the burettes are graduated to hold 100 cc., the contraction, as read upon the tube, will equal the percentage by volume of the oxygen in the air.

It is to be noted in connection with the use of the Hempel gas-analytical apparatus that gases passing rapidly through narrow tubes into those of larger caliber are cooled to some extent and may require a little time to recover their former temperature.

While a gas is confined in a burette care should be taken to have the reservoir so adjusted that the pressure upon the gas is about equal to that of the air. This precaution will reduce to a minimum the errors due to leakage and diffusion.

If a gas is very rich in oxygen, the heat generated by the absorption may cause the phosphorus to melt or even to burst into flames. In such cases the proportion of the oxygen should be gradually reduced by transferring only a part of the gas to the pipette and then immediately withdrawing it. After a few repetitions of this manipulation it is safe to leave the whole body of the gas in contact with the phosphorus, however rich in oxygen it may have been in the beginning.

III. BY ABSORPTION WITH POTASSIUM PYROGALLATE

There are required:

1. A so-called "double absorption pipette," Fig. 61.

2. An alkaline solution of pyrogallol. This is made by mixing in the pipette 5 grams of pyrogallol dissolved in 15 cc. of

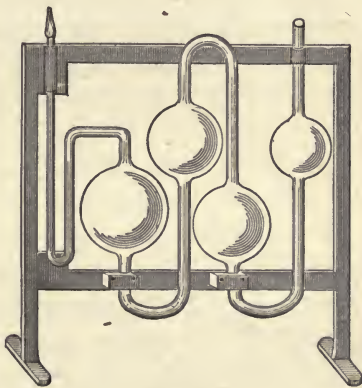


FIG. 61

water and 120 grams of potassium hydroxide dissolved in 80 cc. of water. Potassium hydroxide purified with alcohol must not be used. A solution of the concentration given above liberates no carbon monoxide during the absorption of oxygen. At temperatures above 15° the absorption is moderately rapid, while at lower temperatures it is slow.

Having transferred the air from the burette to the pipette, close the rubber tube upon the latter with a Mohr pinchcock, detach the pipette, and shake it for three minutes. Return the gas to the burette and measure. Repeat the operation until the volume of the residual gas remains constant.

Other reagents which are used for the determination of oxygen in gas mixtures are chromous chloride, and metallic copper in a solution of ammonia and ammonium carbonate.

EXERCISE XLIV

DETERMINATION OF HYDROGEN

I. BY EXPLOSION WITH OXYGEN

Introduce hydrogen, obtained by the method of Bunsen, into the eudiometer, add four times the quantity of air (free from carbon dioxide), and explode. In this instance K will equal 5.



FIG. 62

When hydrogen is to be determined in a case in which air cannot be used owing to the presence of nitrogen in it, the oxygen required for the explosion is obtained from potassium chlorate. A minute retort with a capacity of from 6 to 10 cc., Fig. 62, is blown from a piece of tubing and half filled with the dried and pulverized salt. After filling, the end of the outlet is bent upwards to facilitate the entrance of the oxygen into the eudiometer. Before introducing the gas, the air is expelled from the retort by heating until the evolution of oxygen becomes quite rapid,

and care is taken that the quantity introduced shall not be more than four times that of the hydrogen to be determined.

In the determination of hydrogen in the presence of nitrogen, as in that of oxygen, the proportion of explosive gases to non-explosive must not exceed the ratio of 64 to 100.

II. BY ABSORPTION WITH PALLADIUM

When hydrogen is passed over palladium sponge which is covered with or contains some of the oxide of the metal, the oxide is reduced, and the heat generated by the reaction raises the temperature of the metal to the point at which it absorbs the remainder of the hydrogen with avidity. In this way hydrogen may be separated from nitrogen, carbon dioxide, and methane. According to Hempel, who developed the method, the absorption is not interfered with by water vapor or traces of ammonia, but may be prevented by carbon monoxide, large quantities of the vapors of benzene and alcohol, and by traces of hydrochloric acid. The prevention



FIG. 63

of the occlusion by the last-named substances he supposes to be due to the fact that they appropriate the oxygen of the palladium oxide, but in burning do not generate enough heat to raise the metallic palladium to the temperature at which it can absorb the hydrogen.

If air is passed over palladium which has been employed to absorb hydrogen, the occluded gas is burned to water and a small portion of the metal is at the same time converted into oxide, giving a mixture which is ready for a second absorption.

The palladium tube which is usually employed in determining hydrogen is shown in Fig. 63. The parts *a* and *b* are nearly capillary, while *c* has an internal diameter of about 5 mm. and contains from 2.5 to 3 grams of spongy metal mixed with some oxide. The tube contains air, and its volume must be ascertained before the apparatus can be used for an absorption,

since, in the presence of palladium, hydrogen and oxygen are converted into water and the observed shrinkage in volume will be due not alone to the removal of the former gas, but in part to the disappearance of the oxygen in the air which fills the palladium tube. To determine the volume of the air in the tube, Hempel recommends the following procedure: The apparatus is closed at one end with a short rubber tube and a glass plug, and connected at the other end with a gas burette partly filled with air. The tube is then cooled to 9° by immersing it in water of that temperature, and the volume of the air in the burette is read at atmospheric pressure. Afterwards it is placed in water heated to the boiling point. The expansion of the gas in the burette which follows the raising of the temperature of the air in the palladium tube from 9° to 100° is equal to one-third the capacity of the tube. It is somewhat more accurate, and at the same time more expeditious, to fill a burette with air, to remove the oxygen with pyrogallol, and then to insert the palladium tube between the burette and the pyrogallol pipette, and actually determine the oxygen in it. Or one may insert the palladium tube between a pyrogallol pipette and a burette filled with air, and determine the oxygen. The difference between the whole contraction which takes place and 20.9 per cent of the volume of the air in the burette is the volume of the oxygen in the palladium tube. If either of the last two methods is adopted, the gas must, of course, be passed back and forth until the absorption of the oxygen is surely complete. The same methods may be employed to ascertain the capacity of many small vessels, or the extent of the vacant space in them when they are partly filled.

The determination of hydrogen by absorption is made in the following manner: Having removed other absorbable gases by means of the appropriate reagents, the burette, which may contain nitrogen and marsh gas in addition to hydrogen, is attached to the palladium tube, and the latter is connected in turn with a simple Hempel pipette filled with water. The portion of the

tube containing the mixture of metal and oxide is immersed in water having a temperature of from 90° to 100° , and the gas is passed three times back and forth over the palladium. Finally, the hot water is replaced by cold, and the residual gas — to cool it — is again passed two or three times over the metal.

If a mixture of hydrogen and marsh gas with a considerable excess of air is slowly passed over palladium whose temperature is kept below 200° by surrounding the tube containing it with water, the hydrogen alone is burned.

EXERCISE XLV

ANALYSIS OF ILLUMINATING GAS

(Method of Hempel)

The various constituents of the gas are determined in the following manner and order:

1. The so-called hydrocarbon vapors (principally benzene) are absorbed by alcohol.

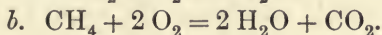
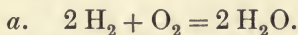
2. The carbon dioxide is absorbed by potassium hydroxide.

3. The heavy (unsaturated) hydrocarbons — ethylene, propylene, etc. — are removed by fuming sulphuric acid.

4. The oxygen, if present, is absorbed by phosphorus.

5. The carbon monoxide is absorbed by an ammoniacal solution of cuprous chloride.

6. A measured portion of the residual gas, which consists of hydrogen, methane, and nitrogen, is mixed with air and exploded. The contraction which follows is due to the reactions:



The carbon dioxide is absorbed by potassium hydroxide. Its volume is equal to that of the methane. The volume of the oxygen which disappears in burning the methane is twice that of the carbon dioxide or that of the methane; hence, if twice

the volume of the carbon dioxide is subtracted from the contraction which follows the explosion, the difference is the contraction due to reaction α , and two-thirds of this is the volume of the hydrogen. The gas remaining after the explosion and the removal of the carbon dioxide is nitrogen.

The apparatus and reagents required are:

1. A Hempel burette filled with water which has been saturated with illuminating gas.

2. A pipette containing 1 cc. of absolute alcohol, but otherwise filled with mercury. The so-called Hempel explosion

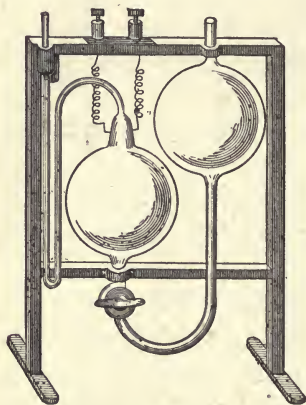


FIG. 64

pipette, Fig. 64, is employed. The pipette is first completely filled with mercury, and the alcohol is run in from a burette at the open end of the small side tube. Before using the alcohol, it must be saturated with the gas. For this purpose about 50 cc. of the gas are drawn in after the introduction of the alcohol and the pipette is closed and shaken for three minutes, after which the residual gas is expelled and the pipette closed.

3. An explosion pipette like 2, containing 1 cc. of water over mercury. The water is introduced and saturated with gas in the same manner as the alcohol in 2.

The alcohol (2) is employed to remove the hydrocarbon vapors, and the water to absorb the vapors of alcohol. The second explosion pipette may be dispensed with; for after the absorption of the hydrocarbon vapors the alcohol may be quickly replaced by an equal volume of water which has previously been saturated with the gas.

4. A "pipette for solid and liquid reagents" for the absorption of carbon dioxide, Fig. 65. The cylindrical bulb is tightly packed with short rolls of iron wire gauze and then filled with caustic potash made by dissolving 1 part of the hydroxide in 2 parts of water.

5. A pipette of the form shown in Fig. 66 for the absorption of ethylene and other unsaturated hydrocarbons by fuming sulphuric acid. The smallest of the three bulbs is filled with glass beads by the maker of the apparatus in order to provide a large absorbing surface for the gas. The function of the beads in

this pipette is the same as that of the wire gauze in the pipette for the absorption of carbon dioxide. All unnecessary exposure of the contents to the air is, of course, to be avoided.

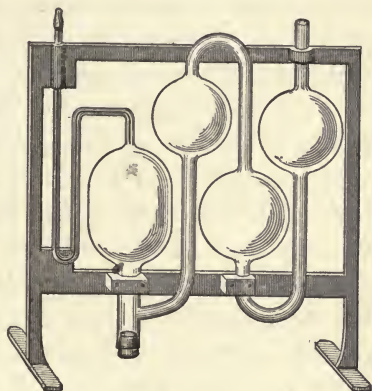


FIG. 65

6. A phosphorus pipette for the absorption of oxygen.

7. Two double pipettes, Fig. 61, filled with an ammoniacal solution of cuprous chloride for the absorption of carbon monoxide. The solution is prepared in the following manner: 10.3 grams of copper oxide are dissolved in from 100 to 200 cc. of commercial concentrated hydrochloric acid. The flask containing the solution is filled with copper wire or wire gauze, and allowed to stand until the liquid becomes colorless. The hydrochloric acid

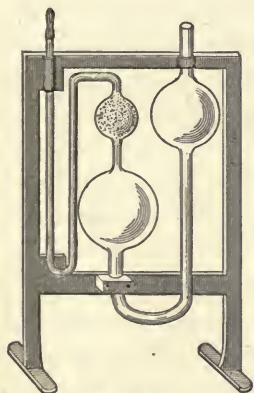


FIG. 66

solution of cuprous chloride is poured into a large beaker containing from 1.5 to 2 liters of cold water. When the precipitated cuprous chloride has subsided, the liquid above is poured

off as completely as possible, and the crystals are washed with 100 or 150 cc. of water into a 250-cc. flask. Ammonia gas is conducted into the flask until the liquid assumes a pale blue color, and no longer. During the treatment with ammonia the flask is to be closed with a doubly perforated stopper, through which pass the ammonia delivery tube and a bent glass tube which dips into a little mercury. For the production of the ammonia gas about 200 cc. of ammonia solution of 0.9 specific gravity will be required. The ammoniacal solution of cuprous chloride is diluted with water to 200 cc. This quantity will suffice for one pipette.

Fill the burette with water through which illuminating gas has been passed for some time, and then with the gas. Before collecting the gas for analysis, however, it should be allowed to waste until it is certain that its composition is no longer affected by the friction in the pipes.

Connect the burette with the alcohol pipette (2), transfer the gas, disconnect, and shake the pipette for three minutes. Return the gas to the burette, transfer it to the water pipette (3), disconnect, and shake for three minutes. Return the gas to the burette and, after waiting three minutes for the water to run down the inner wall of the burette, measure the volume. The contraction, if 100 cc. of the gas were taken, is the percentage volume of the hydrocarbon vapors.

Pass the gas into the caustic potash pipette (4) and withdraw it immediately. Read after three minutes. The contraction is equal to the volume of the carbon dioxide.

Connect the burette with the fuming sulphuric acid pipette (5), using a dry glass tube and dry rubber for the purpose, and taking care not to allow the acid to come in contact with the latter. After absorption, which requires only a short exposure, pass the gas into the caustic potash pipette (4) to remove sulphur dioxide, and withdraw it immediately. Measure after three minutes. The contraction gives the volume of the unsaturated hydrocarbons.

Pass the gas into the phosphorus pipette and allow it to remain there three minutes. Withdraw and read after three minutes.

Pass the gas into one of the cuprous chloride pipettes (7). Disconnect, and shake the pipette for two minutes. Withdraw the gas and transfer it to the second cuprous chloride pipette and shake for three minutes. Return the gas to the burette and measure after three minutes. If the solution of cuprous chloride is perfectly fresh, the treatment of the gas in the second pipette may be omitted. A solution in which a considerable quantity of carbon monoxide has been absorbed will yield up some of that gas whenever another gas in which the partial pressure of carbon monoxide is small is brought in contact with it; hence the practice of using two pipettes, one of which always contains a comparatively fresh solution of cuprous chloride.

Return the gas to the cuprous chloride pipette last used, disconnect the burette and cleanse, and fill it with water not saturated with the gas. Measure into the burette from 12 to 15 cc. of the residual gas and then nearly fill it with air. Transfer the mixture to the explosion pipette (2), taking care to fill the capillary of the pipette with water. Close with a strong pinchcock and insert a glass plug in the open end of the rubber connector. Shake the pipette vigorously, close the glass stopcock, and explode. Open the stopcock and return the gas at once to the burette. Measure and transfer to the caustic potash pipette, returning the gas immediately to the burette. The method of calculating the quantities of methane and hydrogen has already been explained. The nitrogen is found by difference. It is well to pass the gas, after removing the carbon dioxide and measuring, into the phosphorus pipette in order to demonstrate the sufficiency of the supply of oxygen.

If preferred, the hydrogen may, of course, be determined separately by absorbing it in palladium.

Some unfortunate accidents have resulted from the use of the explosion pipette, and the student is warned to insure his

safety by covering the apparatus with a strong box before closing the circuit.

For further information regarding the quantitative determination of gases, the student is referred to the works of Bunsen, Winkler, and Hempel.



CHAPTER XVIII

THE METALS OF THE ALKALIES AND OF THE ALKALINE EARTHS

EXERCISE XLVI

DETERMINATION OF POTASSIUM AS DOUBLE POTASSIUM-PLATINUM CHLORIDE

Weigh about 0.1 gram of pure potassium chloride into a small porcelain dish. Dissolve the salt in a little water and add somewhat more of a nearly neutral solution of platinum chloride than is necessary to precipitate all of the potassium as the double compound. Evaporate upon the water bath to a sirupy consistency. Allow the dish to cool, and add to the contents 10 or 15 cc. of strong alcohol. After mixing, allow the contents of the dish to remain undisturbed for an hour or more and then filter.

If a Gooch filter is available, this should be used. Otherwise filter through a very small paper. Wash with alcohol and allow the paper to dry at the temperature of the air. When dry, remove the precipitate as completely as may be to a weighed platinum or porcelain crucible. Replace the filter in the funnel and dissolve the precipitate remaining upon it in a little boiling water and wash the paper clean, collecting the solution and washings in a small beaker or a porcelain dish. Place the weighed crucible containing the greater portion of the platinum salt upon a water bath and evaporate in it to dryness the solution obtained from the filter paper. Heat to constant weight in an air bath at a temperature of 130°.

After weighing, place a small quantity of pure oxalic acid in the crucible. Heat, with the cover on, gently at first and afterwards more strongly. Weigh and then repeat the treatment with oxalic acid, etc. The residue after such treatment is a mixture of metallic platinum and potassium chloride, $Pt + 2 KCl$. Dissolve out the chloride and weigh the platinum. The same decomposition of the double salt may be effected by heating it in a current of hydrogen.

The double chloride of potassium and platinum is not wholly insoluble in strong alcohol. Therefore proceed with the first filtrate in the following manner: Add to it a small quantity of pure sodium chloride in solution and evaporate at a temperature not exceeding 75° until all of the alcohol has been removed. Add a little platinum chloride. Evaporate on the water bath nearly to dryness. Treat the residue with strong alcohol, etc. The sodium chloride is used to prevent the decomposition of the platinum chloride by the alcohol during the evaporation. More of the platinum chloride is added, before the final treatment with alcohol, in order to convert any excess of sodium chloride into the double sodium-platinum salt, which is soluble in alcohol, while sodium chloride is insoluble. If the last step is omitted, the small quantity of potassium salt which is obtained from the filtrate may be mixed with sodium chloride.

When the salt in which potassium is to be determined is not the chloride, also when other acids or their salts are present, the procedure is somewhat modified. If the acids are volatile ones—e.g. nitric acid, acetic acid, etc.—the solution of the material is repeatedly evaporated with hydrochloric acid before treating with platinum chloride. If nonvolatile acids, like phosphoric and boric acids, are present, the solution is evaporated to a small volume with hydrochloric acid, and then treated with an excess of platinum chloride and a considerable quantity of strong alcohol. After standing for 24 hours, the precipitate is filtered, washed with alcohol, etc.

The determination must, of course, be conducted in an atmosphere which is free from ammonia and from hydrogen sulphide.

According to Fresenius, potassium-platinum chloride is soluble in 12,083 parts of absolute alcohol, and in 3775 parts of 76 per cent alcohol.

THE MONROE FILTER

A filter which is to be recommended for the collection of potassium-platinum chloride and many other precipitates is that proposed by C. E. Monroe (*Chemical News*, 58, 101). It is a modification of the Gooch filter, in which platinum sponge is used in the place of asbestos. The perforated Gooch crucible is placed upon filter or blotting paper and its bottom covered to a depth of 4 or 5 mm. with moist ammonium-platinum chloride. The crucible is cleansed, dried, covered, and placed in its cap, and the double salt is gradually decomposed by heat. If cracks appear in the filter, they may be filled by rubbing down with the smooth end of a glass rod, or by introducing more of the double salt and reheating the crucible. If the crevices are large, it will be found advantageous to employ both of these means of closing them.

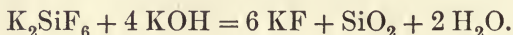
A filter of this kind is useful when the substance is of such a character that a paper upon which it is collected cannot be burned, and also for the filtration of precipitates which are soluble in acids. The oxygen in the spongy platinum must be removed with boiling water before filtering solutions containing hydrochloric acid. Otherwise platinum chloride will be found in the filtrate.

OTHER METHODS OF DETERMINING POTASSIUM

If potassium is in combination with any volatile acid, and is otherwise free from nonvolatile matter, it may be evaporated with hydrochloric, nitric, or sulphuric acid, and weighed as chloride, nitrate, or sulphate. If either of the first two is employed, the evaporation must be repeated with fresh portions of the acid until the weight of the residue is found to be constant.

Potassium may also be precipitated from an alcoholic solution by hydrofluosilicic acid, and subsequently determined by means of a standard solution of potassium or sodium hydroxide.

The concentrated solution of the salt is treated with an excess of hydrofluosilicic acid and an equal volume of strong alcohol. The precipitate is collected upon a filter and washed with a mixture of equal volumes of alcohol and water until a neutral filtrate is obtained. It is then returned, together with the filter, to the beaker in which the precipitation was made, treated with boiling water and titrated with the standard alkali, with use of litmus as the indicator. The reaction which takes place is represented by the following equation:



Free acids, especially sulphuric acid, should be removed by evaporation before attempting to precipitate potassium as the fluosilicate.

EXERCISE XLVII

SEPARATION AND DETERMINATION OF POTASSIUM AND SODIUM

Weigh about 1 gram of pure potassium-sodium tartrate, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, into a platinum dish. Heat very cautiously until all volatile matter has been expelled, and then raise the temperature of the charred residue to a dull red. When cold, add water and heat for some time nearly to the boiling point. Filter through a small, "ashless" paper into a porcelain vessel. Wash the dish, the carbon, and the filter thoroughly with hot water. Return the undissolved material, together with the paper, to the platinum dish, and incinerate at the lowest practicable temperature. The ash should consist of alkaline carbonates except for a minute, hardly weighable, quantity of insoluble matter derived from the paper. Acidify the solution of the alkalis with hydrochloric acid and evaporate it to a small volume in the platinum dish. Pour the liquid into a weighed platinum crucible and

continue the evaporation to dryness, adding from time to time the water used in washing the dish. Heat the crucible for a long time very moderately, then cover it and gradually raise the temperature to a dull red. Weigh the mixed chlorides and dissolve them in water. Transfer the solution to a porcelain dish and add a quantity of platinum chloride which will certainly more than suffice to convert both potassium and sodium into the platinum double salts. Evaporate the solution, at a temperature below the boiling point of water, to a thick liquid. Add strong alcohol and proceed in other respects as directed in Exercise XLVI.

To test the purity of the weighed potassium-platinum chloride, examine it with a magnifying glass and then treat it repeatedly with small quantities of cold water, pouring the solutions thus obtained into a porcelain dish. Add a little more platinum chloride, evaporate, treat with alcohol, etc. The second weight of the double salt should agree very closely with the first. The filtrate from the second precipitation is to be added to the solution containing the sodium salt.

The quantity of the sodium can, of course, be calculated from the weights of the mixed chlorides and of the potassium chloride in the double salt. The result of the calculation is, however, to be confirmed in the following manner: Evaporate the solution containing the sodium salt and the excess of the platinum chloride to dryness in a porcelain crucible. Heat the residue moderately in a current of hydrogen and extract the sodium chloride with water. Evaporate the solution in a weighed platinum crucible, and proceed as in the determination of the weight of the mixed chlorides.

SEPARATION OF POTASSIUM AND SODIUM FROM OTHER SUBSTANCES

When potassium and sodium are to be determined they are first isolated from all other substances in the form of chlorides if practicable. How this may be accomplished when the alkalies

are in combination with nonvolatile organic acids has been learned from the preceding exercise.

The nitrates, bromides, iodides, cyanides, acetates, and, in general, the compounds of the alkalies with the more volatile acids are readily converted into chlorides by repeated evaporation to dryness with hydrochloric acid.

Sulphates, phosphates, borates, and some other salts require a different treatment, and usually such a treatment as will effect a separation of the acid, leaving the alkaline metals in combination with chlorine, or in a condition to be converted into chlorides.

1. SULPHATES

Various methods are employed for the conversion of the sulphates of the alkalies into chlorides. (1) The dry salts are heated in a platinum crucible with ammonium chloride, and the process is repeated until a constant weight is obtained. (2) The solution of the sulphates is treated with a very moderate excess of pure lead acetate and a little alcohol, and filtered. The filtrate is treated with hydrogen sulphide to precipitate the excess of the lead, and again filtered. Finally, the solution, which now contains the potassium and sodium in the form of acetates, is repeatedly evaporated with hydrochloric acid. (3) The precipitation of the sulphuric acid by barium chloride or by strontium chloride and alcohol—a method formerly in use—has been abandoned owing to the tendency on the part of barium and strontium when precipitated as sulphates to carry down with them the salts of the alkalies.

2. PHOSPHATES

Phosphoric acid may be separated from the metals of the alkalies by precipitation either as the phosphate of lead or as the phosphate of iron. (1) The solution is treated with a little ammonium chloride or with hydrochloric acid, and then with lead acetate as long as a precipitate forms. Afterwards there

is added a quantity of lead carbonate, prepared by treating a solution of the acetate with ammonium carbonate. After long digestion the precipitate — consisting of lead phosphate, chloride, and carbonate — is filtered and washed. The lead in the filtrate is precipitated by hydrogen sulphide. The lead sulphide is collected upon a paper and washed, and the filtrate is repeatedly evaporated with hydrochloric acid. (2) The solution is acidified with hydrochloric acid, treated with an excess of ferric chloride, and then considerably diluted with water. Ammonia is added to neutral reaction and the solution is boiled. The precipitate, which contains all of the iron and the phosphoric acid, is filtered, and the filtrate, which contains the potassium and sodium, is, as usual, evaporated with hydrochloric acid.

3. BORATES

Boric acid is separated from the alkaline metals, and also from all other metals, as boron fluoride. The material is digested for some time in a platinum vessel with aqueous hydrofluoric acid, and then cautiously treated with sulphuric acid. The vessel is afterwards heated — moderately at first, but finally to a temperature sufficient for the expulsion of the excess of sulphuric acid. The boron is completely volatilized, while the alkalies remain as sulphates. Boric acid may also be separated from the alkaline and from other metals by converting it into a volatile ethereal salt by treating the borate with sulphuric acid and methyl or ethyl alcohol.

EXERCISE XLVIII

DETERMINATION OF POTASSIUM AND SODIUM IN A SILICATE

Weigh into a platinum dish from 0.7 to 1.0 gram of a soda-potash glass — a fragment of a Florence flask will answer as material — which has been finely pulverized and dried at 100°

or at ordinary temperatures in a desiccator. Treat the powder, little by little, with a fuming aqueous solution of hydrofluoric acid which has been purified by distillation from a platinum retort. Stir the mixture occasionally with a platinum wire or spatula. Warm the dish for some time upon a water bath and then add, drop by drop, sulphuric acid which has been diluted with an equal volume of water until more than enough has been introduced to convert all of the bases into sulphates. Evaporate for a time upon the water bath and then gradually heat to higher temperatures until nearly all of the excess of sulphuric acid has been expelled. Allow the dish to cool, add concentrated hydrochloric acid, and then set it aside for several hours. Dilute with water and warm gently. The material in the dish should dissolve completely. If it does not, filter through an ashless paper, wash, and burn the filter, and treat the residue in the same manner as the original material.

The solution will contain potassium, sodium, and calcium—the principal metallic constituents of the glass—as sulphates, also small quantities of the sulphates of iron and aluminium, and possibly of manganese. Evaporate until the greater portion of the hydrochloric acid has been expelled. Transfer the contents of the dish to a beaker, washing the former well with water. Heat nearly to the boiling point and add a moderate excess of ammonium oxalate and enough ammonia to render the liquid distinctly alkaline. Set the beaker in a warm place and allow it to stand undisturbed for 24 hours. Decant the clear liquid through a small paper, and wash the precipitate in the beaker with several small portions of hot water before allowing it to come upon the paper. Wash well the beaker, and filter without attempting to bring all of the oxalate in the former into the latter. To the filtrate add a few drops of ammonium sulphide. If a precipitate appears, add a little more of the reagent and set aside for several hours. Filter and wash with water containing a small quantity of ammonium sulphide. Acidify the filtrate slightly with sulphuric acid and evaporate to

dryness, first in porcelain and then in a large weighed platinum crucible. Heat the residue cautiously with the cover on the crucible as long as ammonium salts are observed to escape. Allow the crucible to cool, add dry ammonium carbonate, and again heat. Repeat the treatment with ammonium carbonate and the subsequent heating two or three times and then weigh. Dissolve the mixture of sulphates in a little water; the solution should be clear. If it is not clear, the treatment with ammonium oxalate must be repeated, but not that with ammonium sulphide. Add a little ammonium sulphate to the solution, evaporate, and ignite, using ammonium carbonate as before to assist in the removal of the acid in the acid sulphates.

Having found the weight of the mixture of potassium and sodium sulphates, add dry ammonium chloride which contains no nonvolatile matter, and gently ignite. Repeat the addition of ammonium chloride and the ignition until a constant weight is obtained.

Having found the weight of the chlorides, separate and determine the potassium and sodium as directed in Exercise XLVII.

The calcium in the glass should also be determined by heating the oxalate and weighing the resulting carbonate.

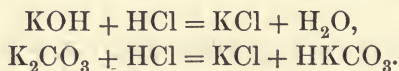
DETERMINATION OF AN ALKALINE CARBONATE IN A CAUSTIC ALKALI

Most caustic alkalies contain more or less of an alkaline carbonate, owing either to the incomplete conversion of the latter in the process of manufacturing of the former, or to the exposure of the product to the carbonic acid of the air. There are various methods of determining the amount of the carbonate in such materials. Of these, the following is the simplest: A weighed quantity of the alkali is dissolved in water and diluted to a known volume. Measured portions of the solution are then withdrawn and titrated with a standard acid, using methyl orange as the indicator. In this way the sum of the caustic

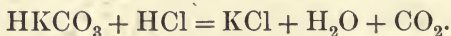
alkali and the carbonate is found. Another weighed portion of the material is dissolved in water, treated with enough barium chloride to precipitate the carbonic acid, and then diluted to a known volume. The measuring flask in which the precipitation was made is closed, shaken, and then set aside until the barium carbonate settles. Measured portions of the clear solution are neutralized with the standard acid, using either phenolphthalein or litmus as the indicator. By the last operation the quantity of the caustic alkali is determined, and the difference between this and the total alkali — previously estimated — is the amount of the carbonate. If great accuracy is required, a correction must be made for the space occupied by the barium carbonate. Its volume may, of course, be found by dividing its estimated weight by its specific gravity.

The alkaline hydroxides and carbonates may be estimated in the same solution in the following manner: The liquid is treated with phenolphthalein and then titrated to neutral reaction with a standard acid. Methyl orange is then added and the titration continued to acid reaction. The equations given below represent the reactions which take place:

1. When acid is added until the phenolphthalein loses its color:



2. When acid is added until the methyl orange reddens:

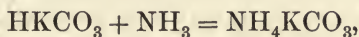


The alkali in the form of carbonate is equivalent to twice the acid used in the last titration.

DETERMINATION OF ACID CARBONATES IN THE PRESENCE OF NEUTRAL CARBONATES

The solution of the material is treated in a measuring flask with a measured but excessive quantity of a dilute standard ammonia and then with an excess of barium chloride. The

flask is filled to the mark with boiled water and the barium carbonate allowed to subside. The excess of the ammonia is ascertained by titrating measured portions of the clear solution with a standard acid. The ammonia added, but not found in the subsequent titration, has disappeared in the reaction,



and each molecule of the missing ammonia represents one molecule of acid carbonate.

If a standard solution of sodium or potassium hydroxide, free from carbonate, is used instead of ammonia, and phenolphthalein is employed as the indicator, the titration of the excess of the alkali may be made in the presence of the barium carbonate, and the trouble of diluting to a known volume avoided.

In the analysis of the cruder commercial products, the probable presence of alkaline sulphides, sulphites, aluminates, and silicates must be taken into account.

EXERCISE XLIX

SEPARATION AND DETERMINATION OF BARIUM, STRONTIUM, AND CALCIUM

(By the methods recommended by Fresenius)

In addition to the more ordinary reagents, there are required :

1. Ammonium chromate. To prepare this, dissolve a weighed quantity of crystallized chromic anhydride in water and treat with ammonia until the solution acquires the characteristic yellow color of the neutral chromates of the alkalies. Add a second equal portion of chromic anhydride, and evaporate the solution to the point of crystallization. Recrystallize the product until the salt gives no reaction for sulphuric acid when reduced by alcohol and hydrochloric acid and treated with barium chloride. Dissolve the pure salt in water and add ammonia until the solution, when diluted, reacts neither acid nor alkaline.

2. Anhydrous ether. Heat the commercial product upon a water bath with thin shavings of clean sodium until the evolution of hydrogen ceases, and then distill. The flask containing the ether must be attached to a return condenser; and as it is unsafe to have a flame in the vicinity, the water employed in the bath should be heated elsewhere and introduced as occasion requires.

3. Absolute alcohol. This may be prepared in either of two ways. First, 95 per cent alcohol is treated with 250 grams per liter of calcium oxide and heated upon a water bath in a flask to which an inverted condenser is attached. After an hour or more, the alcohol is distilled. If it contained in the beginning more than 5 per cent of water, the treatment with lime must be repeated. Or, second, the alcohol is allowed to remain for a long time in contact with anhydrous copper sulphate and is then distilled. The absorption of the water by the sulphate is, of course, greatly facilitated by agitation.

4. Pure barium, strontium, and calcium carbonates. The first two are obtained by treating solutions of the pure chlorides with ammonia and ammonium carbonate, and filtering, washing, and igniting the precipitate in a platinum crucible. Calcium carbonate may be prepared in the same manner, or Iceland spar may be used.

Weigh into a beaker about 0.3 gram of each of the three carbonates. Dissolve with the least practicable quantity of hydrochloric acid and evaporate the solution to dryness to remove the excess of the acid. Dissolve the chlorides in water and dilute to 300 cc. Add half a dozen drops of acetic acid (sp. gr. 1.065), and heat the solution nearly to the boiling point. Add 12 or 15 cc. of a 10 per cent ammonium chromate solution and set aside for an hour or longer. Decant the liquid through a filter. Wash the precipitate with water strongly colored with ammonium chromate until the filtrate gives no precipitate with ammonia and ammonium carbonate, and then with pure warm water until the filtrate gives only a slight red color with silver nitrate. The precipitate contains all of the barium, some

strontium, and a little calcium. Return it, as completely as may be, with the aid of the wash bottle, to the beaker, and dissolve what remains on the filter with a little warm and very dilute nitric acid. Wash the filter into the beaker and dissolve the remainder of the precipitate in the smallest possible quantity of warm dilute nitric acid. Dilute the solution to 200 cc. and heat. Add slowly 5 cc. of ammonium acetate (30 per cent solution) to neutralize the excess of the nitric acid, and then ammonium chromate until the odor of acetic acid disappears. At the end of an hour decant the liquid through a filter. Digest the precipitate remaining in the beaker with hot water. Let it cool and again decant. Bring the precipitate upon the filter with cold water and wash it with the same until the filtrate gives only a slight color reaction with silver nitrate. The precipitate now contains all of the barium (except slight traces), and is free from strontium and calcium. The last filtrate, which contains the strontium and calcium retained by the barium chromate first precipitated, is to be added to the first.

Dry the paper on which the barium chromate is collected, and remove the precipitate to a weighed platinum crucible. Fold the paper loosely, place it in the crucible, and incinerate at a low temperature. Continue gently to ignite until the chromate reduced during the burning of the paper has been reoxidized.

Concentrate by evaporation the filtrate which contains the strontium and calcium, adding a little nitric acid. Treat the solution with ammonia and a moderate excess of ammonium carbonate and allow it to stand for some hours in a warm place. Filter and wash with water. Dissolve the precipitate of strontium and calcium carbonates in nitric acid and evaporate the solution in a porcelain dish. Heat the residue in an air bath for a long time at a temperature of 130°. Grind the dried nitrates to a fine powder with a porcelain pestle. Add 5 cc. of a mixture of equal volumes of ether and alcohol. Grind the materials together quickly and pour the liquid portion, as perfectly as may be, into a small flask. Repeat the extraction five

times. Evaporate the ether and alcohol adhering to the residue, and dry it again at 130° . Transfer it to the flask containing the solution and wash the dish with the mixture of ether and alcohol. Close the flask and agitate the contents from time to time for 24 hours. Filter through a small dry paper and wash well with the ether-alcohol mixture.

The filtrate contains the calcium. Add to it a slight excess of sulphuric acid. After 12 hours collect the precipitate upon a Gooch filter, wash with alcohol, dry, ignite at a very low red heat, and weigh.

Dissolve the strontium nitrate remaining on the filter and in the flask in a small quantity of water. Add to the solution an equal volume of alcohol and a moderate excess of sulphuric acid. After 12 hours collect the precipitate on a filter, wash with a mixture of equal volumes of water and alcohol, dry, ignite, and weigh.

Instead of separating the barium from the other metals and afterwards the calcium from the strontium as prescribed, the mixture of the three carbonates may be converted at once into nitrates and the calcium salt extracted from the dried residue with the mixture of ether and alcohol. The subsequent separation of barium from strontium by means of ammonium chromate would not require any modification in consequence of the absence of calcium.

Within recent years an elaborate examination of all the methods hitherto proposed and in use for the separation of the alkaline earths has been made by Fresenius. As regards the separation of calcium from strontium, only one, the ether-alcohol method, was found to yield satisfactory results. For the separation of barium from strontium and calcium, two methods, in modified forms, were found to be available. One of these, the better of the two, has been presented in the preceding exercise. The other, which is based on the comparative insolubility of barium silicofluoride, is briefly given below.

The solution containing, besides barium, strontium or calcium, or both strontium and calcium, as chlorides, is diluted to

100 cc. and treated with an excess of pure hydrofluosilicic acid. After 12 hours the precipitate is collected upon a filter and washed with cold water until the filtrate gives no reaction for chlorine. The material upon the paper is free from strontium and calcium, but the filtrate contains a small fraction of the barium, possibly amounting to, but not exceeding, 1 part of BaSiF_6 to 3000 parts of the liquid. To the filtrate there is added from five to six times the volume of half-normal sulphuric acid which is estimated to be necessary for the precipitation of the barium, on the assumption that the solution is saturated with the silicofluoride. The precipitate, which is free from calcium but contains a little strontium, is collected upon a filter, washed, dried, and, after burning the paper, converted into carbonate by fusion with sodium carbonate. The carbonates are converted into chlorides and dissolved in a small volume of water. To this solution there is added a small quantity of hydrofluosilicic acid, and 30 minutes later a volume of alcohol equal to one-third the total volume of the solution. The precipitate is collected and washed with alcohol which has been diluted with an equal volume of water. The second precipitate of barium silicofluoride is free from strontium. It is not practicable to determine barium by weighing the silicofluoride. It is therefore necessary to convert the metal in the two precipitates into sulphates. To determine the strontium and calcium in the filtrates, they must be precipitated together as sulphates, converted into carbonates and then into nitrates, separated by the ether-alcohol process, and finally precipitated and weighed as sulphates.

DETECTION OF BARIUM, STRONTIUM, AND CALCIUM

(The process recommended by Fresenius)

When the alkaline earths are separated from magnesium—after removal of all other metals except those of the alkalies—they are always obtained in the form of carbonates. To determine whether the precipitate consists of a single carbonate or

of a mixture of two or of all three of the carbonates, the following method is recommended: The precipitate is dissolved in nitric acid, the solution is evaporated to dryness in a small porcelain dish, and the residue is heated in the dish on an iron plate for 10 or 15 minutes, or until the material no longer smells of nitric acid, and a cold glass plate placed over the dish does not condense any moisture. The temperature of the nitrates may rise to 180° without danger. The dried material is finely ground with a pestle, treated with 5 cc. of a mixture of equal volumes of anhydrous ether and absolute alcohol, and again ground. At the expiration of a few minutes the solution is filtered through a dry paper, and the extraction of the residue is four times repeated with small quantities of the ether-alcohol mixture. Two drops of dilute sulphuric acid are added to the filtrate. If a considerable precipitate forms, calcium is present and need not be searched for further. If, on the other hand, the precipitate is very small, it may be due to the presence of a minute quantity of strontium, and the examination for calcium must be continued. The solution is therefore diluted with about 4 cc. of water and the ether and alcohol are removed by evaporation. The residual solution is treated with a few drops of ammonia and about 1 gram of ammonium sulphate, heated to the boiling point, and filtered through a small paper. The filtrate is slightly acidified with acetic acid and treated with a small quantity of ammonium oxalate. If calcium is present, a precipitate of oxalate will form — immediately if the quantity is considerable, but slowly if it is minute.

The nitrates of barium and strontium are dissolved in 100 cc. of hot water and the solution is heated to the boiling point. There are then added 3 or 4 drops of acetic acid and, very gradually, a solution of neutral potassium chromate until the liquid exhibits a yellow color. The liquid is again heated to the boiling point. If the odor of acetic acid is perceived, more chromate is added until it disappears. If barium is present, a yellow precipitate will appear — immediately or after a short

interval, according to the quantity in the solution. After an hour the liquid is filtered, and a fraction of the filtrate is treated with small quantities of ammonia and ammonium carbonate. If a considerable precipitate is formed, strontium is present. If no precipitate appears, or only a very small one, the remainder of the filtrate is treated with 1 or 2 drops of nitric acid, evaporated to a volume of 10 or 20 cc., and treated with ammonia and ammonium carbonate. If no precipitate appears, strontium is absent. A minute precipitate, on the other hand, may consist of strontium carbonate or possibly of the calcium salt. Such a precipitate is filtered, washed, and dissolved in a few drops of hydrochloric acid. The solution is evaporated to dryness and the residue is dissolved in from 1 to 2 cc. of a mixture of 3 parts of water and 1 part of alcohol. Finally, there is added to the alcoholic solution 1 drop of potassium chromate, and the liquid is heated just to the boiling point. If strontium is present, a yellow precipitate will appear, either immediately or after a short time.

An account of the recent important investigation of Fresenius on the analytical chemistry of the alkaline earths will be found in the *Zeitschrift für analytische Chemie*, **29**, 20, 143, and 413; **30**, 18, 452, and 583; **32**, 189 and 312.

THE QUANTITATIVE DETERMINATION OF THE INDIVIDUAL ALKALINE EARTHS

1. BARIUM

1. As Sulphate. To determine barium as sulphate, the solution — which should be dilute and free from any large quantity of acid — is heated to the boiling point and treated, with constant stirring, with a moderate excess of dilute sulphuric acid. The liquid is maintained for a long time at a temperature near the boiling point, and then set aside to settle. The clear liquid

is poured through a small paper, if a Gooch filter is not available, and the residue is washed several times by decantation with hot water containing a little sulphuric acid. The precipitate is then brought upon the filter and washed with boiling water until the filtrate gives no reaction for sulphuric acid when treated with barium chloride. The dried precipitate is transferred to a weighed platinum crucible, the paper incinerated in the usual manner, and the ash added to the main portion of the sulphate. The crucible is then heated for a long time over a Bunsen burner in order to reoxidize the barium sulphide formed during the burning of the paper. If the formation of oxide is feared, the ash may be moistened with a very minute quantity of sulphuric acid and the excess of the acid expelled by heat, with or without the aid of ammonium carbonate.

When precipitated from a cold solution, especially in the absence of hydrochloric acid or ammonium chloride, the sulphate is apt to pass through the filter. It is also inclined to carry down with it and to retain with great tenacity other salts, particularly the nitrates. For this reason it is best to evaporate solutions containing nitrates with hydrochloric acid before attempting to precipitate barium as sulphate. The precipitation, together with the sulphate, of certain substances, notably iron, can be largely prevented by the addition of a considerable quantity of hydrochloric acid, but the excess of the sulphuric acid used to precipitate the barium must then be increased in order partially to overcome the solvent action of the hydrochloric acid on the sulphate. In general, the solubility of the sulphate in hydrochloric acid diminishes in proportion to the excess of free sulphuric acid (Fresenius). The salts which are precipitated with barium sulphate may be removed from it—provided their bases do not also form insoluble sulphates—by dissolving the precipitate in concentrated sulphuric acid and pouring the solution into water. The second precipitation of the sulphate is pure. This course should be taken whenever barium is precipitated as sulphate for the purpose of separating

it from the alkalies. In precipitating barium as sulphate, the quantity of sulphuric acid which is added should never be less than will suffice for the conversion of all the bases in the solution into sulphates, and it should considerably exceed this amount whenever the quantity of other acids is large. According to Fresenius, barium sulphate, under the ordinary conditions of precipitation, is soluble in about 400,000 parts of water.

2. As Carbonate. The dilute solution is treated with ammonia and then with a moderate excess of ammonium carbonate. After several hours the precipitate is collected upon a filter, washed with water containing a little ammonia, and ignited over a Bunsen burner in a platinum crucible. If the filter is burned in the crucible without removal of the precipitate, instead of in a wire, or if barium in combination with an organic acid is to be determined as carbonate by burning off the combustible matter, the residue after ignition must be moistened with a concentrated solution of ammonium carbonate, the liquid evaporated, and the carbonate reignited.

Barium carbonate is soluble in 14,137 parts of cold and 15,421 parts of hot water, and is much more soluble in water containing ammonium chloride or nitrate (Fresenius). It is soluble in 141,000 parts of water containing ammonia and ammonium carbonate. If barium is to be separated from the alkalies, it is better to precipitate it as carbonate than as sulphate.

3. As Chromate. The method by which barium is precipitated as chromate for the purpose of separating it from strontium and calcium has already been given. The process is not materially different when the other alkaline earths are absent, except as regards the repetition of the precipitation. The solution of the barium salt is diluted to about 200 cc., heated to the boiling point, and treated with an excess of ammonium chromate. If the solution was previously acid, ammonia is added until a neutral or slightly alkaline reaction is obtained. The precipitate is collected upon a paper, washed first with water containing a little ammonium chromate, then with clear cold water,

dried, and transferred to a weighed platinum crucible. The paper is loosely folded, placed in the crucible, and burned. The contents of the crucible are then heated over a Bunsen burner until the chromate reduced by the burning paper has been reoxidized. A Gooch filter is, of course, to be preferred to one of paper.

The chromate, before ignition, is soluble in 87,000 parts of cold and 23,000 parts of boiling water. Its solubility is increased by the presence of ammonium salts and very markedly by that of acetic acid. The ignited salt is soluble in 160,000 parts of water. In water containing an excess of ammonium or potassium chromate, whether ammonium salts are present or not, it is quite as insoluble as barium sulphate.

When dried to a constant weight at 110° , barium chromate still contains about 0.5 per cent of water. It can be gently ignited without decomposition, but loses weight at a bright red heat. The chromate which is reduced by the burning of a filter upon which it has been collected is reoxidized when heated in contact with the air.

4. As Silicofluoride. Barium silicofluoride is soluble in about 3800 parts of cold and 1200 parts of boiling water. Its solubility is greatly increased by the presence of hydrochloric acid and of ammonium salts, and greatly diminished by the presence of alcohol, especially if there is also present an excess of hydrofluosilicic acid. According to Fresenius, 1 part of the salt dissolves: at 14.5° , in 37,219 parts of a mixture of equal volumes of alcohol (96 per cent) and water; at 15° , in 16,914 parts of a mixture of 1 volume of alcohol and 3 volumes of water; at 15° , in 5263 parts of a mixture of 25 volumes of alcohol, 74.1 volumes of water, and 0.9 volume of 20 per cent hydrochloric acid; at 18° , in 70,679 parts of a mixture of 25 volumes of alcohol, 73 volumes of water, 0.9 volume of 20 per cent hydrochloric acid, and 1.1 volume of 3.7 per cent hydrofluosilicic acid.

Dried to a constant weight at 100° , the salt still contains a quantity of water which varies somewhat according to the conditions under which it was precipitated. At elevated

temperatures it is decomposed. It is therefore not practicable to determine barium by weighing the silicofluoride. The silicofluoride may, however, be converted into sulphate in the following manner: The precipitate, after being washed and dried, is removed from the filter. The filter is burned in a platinum crucible, and to the ash is added the precipitate. The contents of the crucible are treated with concentrated sulphuric acid and heated, first upon a water bath and then upon a sand bath, to expel the excess of sulphuric acid. The residue is treated with hydrofluoric and sulphuric acids and again heated to remove any silica which may have separated during the decomposition of the silicofluoride.

The precipitation of barium as silicofluoride, rather than as sulphate, carbonate, or chromate, will not be found advantageous except as a means of effecting a separation from strontium and calcium; and even for this purpose the silicofluoride process is distinctly inferior to the chromate method.

2. STRONTIUM

1. As Sulphate. The rather concentrated solution of the strontium salt, which should be free from any considerable quantity of hydrochloric or nitric acid, is treated with an excess of dilute sulphuric acid, and then with not less than an equal volume of alcohol. After 12 hours the precipitate is collected upon a filter and washed with a mixture of equal volumes of alcohol and water until a neutral filtrate is obtained. The precipitate must be removed as perfectly as possible from the filter before incinerating the latter, and the former must be thoroughly dried at a moderate temperature before the final ignition. The first precaution is rendered necessary by the volatility of strontium compounds in the flame of a Bunsen burner, and the second by the liability of the sulphate, when not fully dried, to suffer loss in weight in consequence of mechanical transportation by the escaping vapors.

Strontium cannot, of course, be precipitated as sulphate in the manner described when the solution contains other substances which are insoluble or very difficultly soluble in from 40 to 50 per cent alcohol. In such cases the strontium should be precipitated as carbonate as directed under 2.

Strontium sulphate is soluble in 6895 parts of cold and in 9638 parts of boiling water (Fresenius). In water containing free sulphuric acid it is decidedly less soluble (11,862 parts of cold water) than in pure water. Its solubility is greatly increased by the presence of hydrochloric or nitric acid, but not by that of acetic acid. Chlorides of the alkalies and also of magnesium increase its solubility in water; hence the quantity of sulphuric acid which is added for the purpose of precipitating strontium should always be sufficient to convert all chlorides of other metals in the solution into sulphates. In 50 per cent alcohol strontium sulphate is nearly insoluble. Like barium sulphate, the strontium salt is inclined, though to a less extent than the former, to carry down with it and to retain other compounds. It is stable at a red heat and is completely converted into carbonate at ordinary temperatures by ammonium or other alkaline carbonates. The conversion into carbonate is complete notwithstanding the presence of considerable quantities of the sulphate of the alkalies, and is hastened by the application of heat. The difference between barium and strontium sulphates in respect to their conduct towards the carbonates of the alkalies does not, however, afford a means for the quantitative separation of the two metals. If the mixed sulphates are treated with ammonium carbonate or with a solution of potassium carbonate and sulphate, a portion of the strontium sulphate is not converted into carbonate when the barium sulphate is in excess, while, on the other hand, some of the barium sulphate is changed into carbonate when the strontium sulphate predominates in the mixture.

2. As Carbonate. The dilute solution of the strontium salt is treated with ammonia and then with a moderate excess of

ammonium carbonate. After some hours the precipitate is collected upon a filter, washed with water containing a little ammonia, and ignited.

Strontium carbonate is soluble in 18,045 parts of water at ordinary temperatures, and in 56,545 parts of water to which ammonia and ammonium carbonate have been added (Frese-nius). It is dissolved to a considerable extent by ammonium chloride and nitrate, but is reprecipitated from such solutions by ammonia and ammonium carbonate.

3. CALCIUM

1. As Sulphate. The solution, which must contain no salts insoluble in 60 or 70 per cent alcohol, is treated with a slight excess of dilute sulphuric acid, and then with three or four times its volume of alcohol. After 12 hours the precipitate is collected upon a filter, washed with alcohol, and heated to a dull red. If a paper has been used as a filter, the ash should be moistened with sulphuric acid or with a solution of ammonium sulphate before the final ignition.

Calcium sulphate is soluble in 430 parts of cold and in 460 parts of boiling water. Hydrochloric and nitric acids, also ammonium chloride, sodium sulphate and chloride, increase its solubility in water. It is quite readily soluble in hot solutions of ammonium sulphate and sodium thiosulphate, in which the corresponding barium and strontium salts are insoluble. Methods for the separation of calcium from barium and strontium, based on this difference in the conduct of the sulphates, have not, however, proved satisfactory. Like the corresponding salt of strontium, calcium sulphate is readily converted into carbonate by solutions of the carbonates of the alkalies, but calcium cannot thereby be separated from barium, whose sulphate is not attacked by alkaline carbonates.

Calcium sulphate is stable at a low red heat, but at higher temperatures it is converted into oxide.

2. As Carbonate, through Precipitation with Ammonium Carbonate. The solution is treated with ammonia and an excess of ammonium carbonate, and the precipitate, after collection upon a filter, is washed with water to which ammonia has been added. The carbonate is only gently ignited, owing to the danger of converting it into oxide, and before weighing it should be moistened with a concentrated solution of ammonium carbonate, slowly dried, and finally heated to a temperature just sufficient for the volatilization of the ammonium salt.

Calcium carbonate is soluble in 28,500 parts of water and in 65,000 parts of water containing ammonia and ammonium carbonate. It is more soluble in water containing ammonium salts, but is reprecipitated from such solutions by ammonia and ammonium carbonate. Neutral salts of potassium and sodium, also of calcium and magnesium, increase somewhat its solubility. It is stable at a low red heat, but is converted into oxide at higher temperatures.

3. As Carbonate or Oxide, through Precipitation by Ammonium Oxalate. The hot solution of the calcium salt is treated with an excess of ammonium oxalate and then with ammonia to alkaline reaction. After standing in a warm place for not less than 12 hours—at all events until the supernatant solution is perfectly clear—the liquid is poured through a filter without disturbing the precipitate in the bottom of the vessel. The residue is washed several times by decantation with hot water—care being taken to allow each portion of the liquid to pass through the paper before adding another—and then brought upon the filter. If portions of the precipitate adhere to the glass so firmly that they cannot be detached, they are dissolved in a little hydrochloric acid, the solution is transferred to a small vessel, and the oxalate reprecipitated by the addition of ammonia. After settling, the second precipitate is brought upon the filter in the same manner as the first. The oxalate is washed with hot water, dried, and removed to a weighed platinum crucible. The filter paper is burned in a platinum wire and the

ash is also placed in the crucible. The oxalate is heated very moderately for a long time and afterwards to a dull red heat, until the mass, on cooling, appears perfectly white. The material, which may now contain some oxide, is moistened with a concentrated solution of ammonium carbonate, slowly dried, and very gently ignited. The treatment with ammonium carbonate, etc., must be repeated until a constant weight is obtained. It is practicable, though not advantageous, to convert the carbonate into and to weigh the calcium as oxide.

Precipitated calcium oxalate is exceedingly finely divided, and is apt to give trouble by passing through the filter. It is for this reason that the oxalate is never filtered until the precipitate has completely subsided, and that it is washed as far as practicable by decantation. Its solubility in water, which is very slight, is not affected by the presence of the chlorides of the alkalies or of the alkaline earths. Magnesium chloride, on the other hand, increases its solubility to a marked degree; hence in precipitating calcium by ammonium oxalate, enough of the latter should be added also to convert any magnesium which may be present into the oxalate. Dried to a constant weight at 100° , the salt still contains 1 molecule of water of crystallization.

Calcium oxalate may be determined, either directly or indirectly, by potassium permanganate. To determine it directly, the well-washed and still moist precipitate is returned to the beaker and treated with an excess of dilute sulphuric acid. The solution is diluted to 150 or 200 cc., heated to 60° , and then titrated to color with a dilute standard solution of potassium permanganate. To determine it indirectly, the calcium salt is treated in a graduated flask with a measured but excessive quantity of a standard solution of oxalic acid, and then with ammonia to alkaline reaction. The liquid is heated to the boiling point and then allowed to cool. The flask is filled to the mark with water, shaken well, and its contents filtered through a dry paper. Finally, measured portions of the filtrate are heated to 60° , acidified with sulphuric acid, and titrated with permanganate.

CHAPTER XIX

THE ALKALINE EARTHS (CONTINUED) AND MAGNESIUM

THE SEPARATION OF THE ALKALINE EARTHS FROM THE ACIDS

The only acids which require mention in this connection are those with which the metals form insoluble salts or those which must be removed before the metals can be precipitated from their solutions by some particular reagent.

1. SULPHURIC ACID

The sulphates of strontium and calcium, when free from barium sulphate, are readily and completely decomposed at ordinary temperatures by neutral ammonium carbonate. All three of the sulphates are converted into carbonates by a boiling solution of sodium carbonate. But in the case of the barium salt the decomposition cannot be completed in the presence of any considerable quantity of a soluble sulphate; hence it is necessary, after boiling for a time, to pour off the liquid and to repeat the treatment with fresh portions of the alkaline carbonate. It is better, however, when sulphuric acid is to be separated from the alkaline earths, to mix the finely pulverized sulphates in a platinum crucible with four or five times their weight of potassium-sodium carbonate, and to fuse the mixture. If the fused mass is treated with hot water until all soluble matter is dissolved, and the insoluble carbonates are collected upon a filter and thoroughly washed, the separation of the sulphuric acid is complete.

2. PHOSPHORIC ACID

Whether the presence of phosphoric acid is objectionable or not depends upon the form in which it is proposed to precipitate the alkaline earths. If they are to be precipitated from acid solutions as sulphates, the phosphoric acid may remain; while if the precipitation is to be made in a neutral or alkaline solution, e.g. as carbonate, oxalate, chromate, etc., it must be removed.

Unlike sulphuric acid, phosphoric acid cannot be quantitatively separated from barium, strontium, and calcium, either by boiling with a solution of an alkaline carbonate or by fusion with the dry carbonates. The separation may, however, be effected by precipitation of the acid in various ways.

1. The phosphates are dissolved in the slightest possible excess of nitric acid. The solution is treated with a little ammonium chloride, then with lead acetate as long as a precipitate forms, and finally with precipitated lead carbonate. After digesting for some time, the precipitate is collected and washed. The filtrate, which contains the alkaline earths, also the alkalis if any were present, and some lead salts, is treated with a rapid current of hydrogen sulphide and quickly filtered.

2. The phosphates are dissolved, as in the preceding case, with the least possible excess of nitric acid. The filtrate is treated with silver nitrate, and then with silver carbonate until a neutral reaction is obtained. The precipitate is collected and washed, and the silver in the filtrate is removed by hydrochloric acid. This process, like the preceding one, separates the alkalis as well as the alkaline earths from phosphoric acid.

3. The phosphates are dissolved in a porcelain dish with nitric acid. There is then added a quantity of pure mercury which is somewhat greater than will dissolve in the excess of nitric acid. The solution is evaporated to complete dryness upon a water bath. The residue is moistened with a very small quantity of water and again dried, and the operation is repeated

until no clouds form when a glass rod wet with ammonia is held over the dish. The residue is digested with either hot or cold water, collected upon a filter, and thoroughly washed. The filtrate contains, in addition to the metals from which the phosphoric acid has been separated, a small quantity of mercury compounds which must be removed. To this end the solution is evaporated to dryness in a platinum dish and the residue is very gently ignited for a long time. If metals of the alkalies are present, the contents of the dish should be treated from time to time with pieces of solid ammonium carbonate to prevent the formation of alkaline oxides from the nitrates, which would attack the platinum.

This method of Rose effects a satisfactory separation of phosphoric acid, not only from the alkaline earths and the alkalies, but also from all other metals except iron, aluminium, and mercury.

3. HYDROFLUORIC ACID

The only compound which need be considered in this place is the frequently occurring mineral, calcium fluoride, which presents some analytical difficulties.

1. The usual method of separating fluorine from calcium, when a direct determination of the former is not to be attempted, is as follows: The pulverized material is treated in a platinum crucible with an excess of concentrated sulphuric acid, which is afterwards evaporated. The fluorine escapes as hydrofluoric acid while the calcium remains as sulphate. This method of separating fluorine from a metal is applicable to many other fluorides than the calcium salt, but not to all. Some fluorides containing aluminium resist the action of concentrated sulphuric acid. Such substances may, however, be decomposed by fusion with acid potassium sulphate.

If a fluoride contains silica or a silicate, or if one of these is mingled with it, it is decomposed by concentrated sulphuric acid with evolution of silicon fluoride instead of hydrofluoric

acid. This fact is often utilized for the separation and also for the determination of fluorine.

2. If calcium fluoride is heated with a dry alkaline carbonate, the mixture fuses easily to a clear liquid. But on treating the mass with water, the compound is found to be only slightly decomposed. But if calcium fluoride is fused with the carbonate in the presence of silica, the decomposition is complete and the solution obtained by treating the mass with water contains all the fluorine and also the silica in combination with an alkali, while the calcium remains as carbonate.

THE SEPARATION OF THE ALKALINE EARTHS FROM THE ALKALIES

The dilute solution—which should be nearly free from ammonium salts—is treated with a little ammonia and then with a slight excess of ammonium carbonate. After standing for an hour or more in a warm place, the precipitate is collected upon a filter and washed with water to which has been added a little ammonia.

If magnesium is also present, as usually happens in practice, enough ammonium chloride must be added to the solution to prevent the precipitation of magnesium carbonate.

The carbonates of the alkaline earths are somewhat soluble in water containing ammonium chloride or nitrate, though much less so in the presence of ammonia and ammonium carbonate. Of the three, barium carbonate is the most, and strontium carbonate the least, soluble. The filtrate may therefore contain, in addition to the alkalies, weighable quantities of barium and calcium. To remove these, the filtrate is treated with 3 or 4 drops of dilute sulphuric acid, and somewhat later with a little ammonium oxalate. After standing for 12 hours in a warm place, the precipitate, if one appears, is collected and washed with water. The residue on the filter will contain the barium as sulphate and the calcium as oxalate, and it may also contain

a little magnesium oxalate. It is treated with hydrochloric acid and the undissolved barium sulphate is washed with water. The filtrate is neutralized with ammonia to reprecipitate the calcium and to separate it from the small quantity of magnesium which may be present. The calcium oxalate, after standing the usual length of time, is collected and washed and the filtrate is added to that which contains the alkalies and the greater portion of the magnesium. The small quantities of barium and calcium recovered in this way are determined independently, while the main body of the alkaline earths is treated as directed under Exercise XLIX.

If magnesium is absent, the alkalies are isolated in the form of chlorides and separated in the usual manner by means of platinum chloride. If magnesium is present, it must be removed before proceeding to the separation and determination of potassium and sodium.

The method just given provides for the separation from the alkalies of any one or all of the alkaline earths. Barium and calcium, if either occurs without the other and without strontium, may also be separated from the alkalies by other methods. If of the alkaline earths barium only is present, the solution is treated with a quantity of dilute sulphuric acid which will suffice for the precipitation of the barium and also for the conversion of the metals of the alkalies into sulphates. The precipitate is collected, washed, dried, dissolved in concentrated sulphuric acid, and reprecipitated by dilution with water. The solution and reprecipitation of the barium sulphate are necessary in order to recover the alkalies which are carried down during the first precipitation and which cannot be removed from the precipitate by washing. If only calcium is present, the separation may be effected by precipitation with ammonium oxalate in the usual manner.

THE DETERMINATION OF MAGNESIUM

Magnesium is usually determined as pyrophosphate in the following manner: The solution is treated with ammonium chloride and then with an excess of ammonia. If a precipitate appears, it is dissolved by adding more ammonium chloride, or it is dissolved with hydrochloric acid and the solution is again made alkaline with ammonia. The clear liquid is then treated with sodium phosphate, care being taken while stirring not to allow the stirrer to come in contact with the beaker glass. After 12 hours the precipitate is brought upon a filter — with the aid of portions of the filtrate — and washed with a mixture of 3 parts of water and 1 part of ammonia (sp. gr. .96) until the filtrate gives no reaction for chlorine. The precipitate is removed as perfectly as possible from the filter to a *porcelain* crucible. The paper is burned in a platinum wire and the ash added to the main portion of the phosphate. The crucible is heated for a long time at a moderate temperature, afterwards to redness, and finally over the blast lamp. If the pyrophosphate has a gray color, it should be treated with nitric acid and reheated.

If it is desired to avoid the presence of sodium in the filtrate, a solution of ammonium phosphate ($\text{H}(\text{NH}_4)_2\text{PO}_4$) or of phosphoric acid may be employed to precipitate the magnesium.

The precipitated salt has the composition $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, which on ignition yields $\text{Mg}_2\text{P}_2\text{O}_7$. It is soluble in about 15,000 parts of cold water, but is much less soluble in water containing ammonia. Its solubility, even in water containing ammonia, is increased by the presence of ammonium chloride and diminished by that of a soluble phosphate.

If a solution contains no other nonvolatile matter than magnesium, the latter may be determined as sulphate by evaporating with sulphuric acid and gently igniting the residue.

THE SEPARATION OF MAGNESIUM FROM THE ALKALIES

The method here recommended is applicable only to the chlorides. If, therefore, the metals are not already in the form of chlorides, or if other acids than hydrochloric acid are present, the solution is evaporated to dryness in a porcelain crucible and the residue is heated repeatedly with small portions of ammonium chloride, care being taken, in the final heating at least, to volatilize all the excess of the ammonium salt. The dried material, consisting of chlorides and possibly of some magnesium oxide, is treated with a little warm water and then with a quantity of pure mercuric oxide suspended in water which is somewhat more than sufficient to precipitate all the magnesium as oxide. The crucible is heated on the water bath until the contents appear to be dry, and then for a long time to a somewhat higher temperature. The crucible is afterwards covered and more strongly heated in a good draught until all of the mercuric chloride has been expelled. The residue consists of the chlorides of the alkalies, magnesium oxide, and some mercuric oxide. It is treated with hot water and filtered. The insoluble matter is washed with hot water and dried. The paper, without removal of the contents, is rolled up and burned in a weighed crucible. Finally, the magnesium oxide is heated to expel the remaining mercuric oxide. Care must, of course, be taken to avoid inhaling the poisonous vapors of mercury and its compounds.

The filtrate contains the alkalies as chlorides, and these are separated and determined in the usual manner.

OTHER METHODS OF SEPARATING MAGNESIUM FROM THE ALKALIES

1. By Means of Ammonium Phosphate. The solution is treated with ammonium chloride, an excess of ammonia, and a slight excess of ammonium phosphate. The magnesium is precipitated

as ammonium-magnesium phosphate, and is weighed as the pyrophosphate. The filtrate contains the alkalies and also phosphoric acid, which must be removed by one of the methods already given, before the potassium and sodium can be separated and determined.

2. By Means of Barium Hydroxide. The neutral solution—which must be free from ammonium salts—is treated with a solution of barium hydroxide as long as any precipitate forms, and is then heated to the boiling point. The precipitate, consisting of magnesium hydroxide and possibly also of barium sulphate and carbonate, is collected upon a filter and washed with boiling water. It is then dissolved in hydrochloric acid, and the barium is precipitated as sulphate and the magnesium as ammonium-magnesium phosphate.

The filtrate contains the alkalies, the soluble compounds of barium, and, owing to the solubility of the hydroxide in water containing salts of the alkalies, a small quantity of magnesium. The barium is precipitated as carbonate or sulphate while the magnesium is recovered by the mercuric oxide method, or neglected, according as exact or only approximate results are required.

3. By Means of Calcium Hydroxide. The solution is treated with pure calcium hydroxide suspended in water, and heated to the boiling point. After filtering and washing, the calcium and magnesium in the precipitate are separated by means of ammonium oxalate. The calcium in the filtrate is separated from the alkalies by precipitation as carbonate or as oxalate. A small portion of the magnesium will be found with the alkalies, owing to the effect of the salts of the latter upon the hydroxide of the former.

There are still other methods of separating magnesium from the alkalies. One of them is based on the fact that, under certain conditions, magnesium can be precipitated as a double ammonium-magnesium carbonate; another upon the fact that when magnesium chloride is heated with oxalic acid it is converted into oxide.

THE SEPARATION OF MAGNESIUM AND BARIUM

1. By Precipitation of the Barium as Carbonate. The dilute solution is treated with ammonium chloride until ammonia gives no precipitate, then with an excess of ammonia, and finally with a slight excess of ammonium carbonate. After standing (covered) for an hour in a moderately warm place, the liquid is filtered and the precipitate is washed with water containing a little ammonia.

The barium carbonate upon the filter may contain a little ammonium-magnesium carbonate. It is therefore dissolved in hydrochloric acid, and the barium is precipitated as sulphate in the usual manner. The filtrate from the sulphate is evaporated to dryness, the residue dissolved in water, and the little magnesium in the solution is precipitated as ammonium-magnesium phosphate.

The first filtrate — that containing the greater portion of the magnesium — contains a little barium owing to the solubility of barium carbonate in the presence of ammonium salts. It is therefore treated with 3 or 4 drops of dilute sulphuric acid and the minute precipitate is collected upon the same filter with the larger quantity of barium sulphate. The magnesium in the filtrate is precipitated as ammonium-magnesium phosphate, which is collected with that recovered from the barium carbonate.

2. By Precipitation of the Barium as Sulphate. The barium is precipitated as sulphate in the usual manner, and the magnesium in the filtrate is precipitated as ammonium-magnesium phosphate. If barium and magnesium are the only metals to be separated, i.e. if other alkaline earths and the alkalis are absent, the second method is to be preferred to the first.

THE SEPARATION OF MAGNESIUM FROM STRONTIUM

1. By Precipitation of the Strontium as Carbonate. The procedure is precisely the same as for the separation of magnesium and barium. It is to be remarked, however, that the filtrate

from the carbonate contains only traces of strontium, and it need not therefore be treated with sulphuric acid, or rather, with sulphuric acid and alcohol.

2. By Precipitation of the Strontium as Sulphate. There are added to the solution of the salts of the two metals one-half its volume of alcohol, and a quantity of dilute sulphuric acid which will more than suffice to convert both into sulphates. After 12 hours the precipitate is collected on a filter and washed with water to which has been added one-third its volume of alcohol. The strontium is weighed as sulphate. The alcohol in the filtrate is evaporated at a low temperature and the magnesium is precipitated as ammonium-magnesium phosphate.

THE SEPARATION OF MAGNESIUM FROM CALCIUM

1. By Precipitation of the Calcium as Carbonate. As far as the precipitation of the calcium is concerned, the procedure is the same as in the separation of magnesium from barium or strontium. To recover the small quantity of magnesium which may be precipitated with the calcium carbonate, the precipitate is dissolved and the calcium reprecipitated either by ammonium oxalate or by sulphuric acid and alcohol. Since calcium carbonate is somewhat soluble in water containing ammonium chloride, the filtrate — the first one — will contain a little calcium. To recover this, the filtrate is treated with enough ammonium oxalate to convert both calcium and magnesium into oxalates. After 12 hours the precipitate is collected and washed. It consists mainly of calcium oxalate, but may contain a little magnesium oxalate. To remove this, the precipitate is dissolved in hydrochloric acid, and the calcium is reprecipitated by adding ammonia and a small quantity of ammonium oxalate.

2. By Precipitation of the Calcium as Oxalate. The dilute solution is treated with ammonium chloride until ammonia gives no precipitate, then with a slight excess of ammonia, and finally with enough ammonium oxalate to convert both magnesium and

calcium into oxalates. If less of the last reagent is added, the precipitation of the calcium will be incomplete, owing to the solubility of its oxalate in a solution of magnesium chloride. After 12 hours the precipitate is collected and washed. It will contain a little magnesium oxalate. It is therefore dissolved in hydrochloric acid and the calcium reprecipitated by adding ammonia and a small quantity of ammonium oxalate.

The two filtrates, which contain all the magnesium and no weighable quantity of calcium, are evaporated to dryness in a platinum dish and the ammonium salts are expelled by heat. The nonvolatile residue is dissolved in hydrochloric acid, and the magnesium is precipitated in the usual manner by sodium or ammonium phosphate.

THE SEPARATION OF MAGNESIUM FROM BARIUM, STRONTIUM, AND CALCIUM

The method is necessarily a combination of the processes by which magnesium is separated from the individual alkaline earths. The dilute solution, which is, of course, free from sulphuric acid and from phosphoric or any other acid which forms with the metals compounds insoluble in neutral or alkaline solutions, is treated with ammonium chloride until ammonia gives no precipitate, then with ammonia to distinctly alkaline reaction, and finally with a slight excess of ammonium carbonate. The beaker is covered and allowed to stand in a warm place for one hour. The precipitate is collected upon a filter and washed with water to which a little ammonia has been added.

The precipitate contains, in addition to the carbonates of the alkaline earths, a small quantity of ammonium-magnesium carbonate. If the magnesium thus precipitated cannot be neglected, the mixture of carbonates must be dissolved in hydrochloric acid and the alkaline earths reprecipitated with sulphuric acid and alcohol. The filtrate from the sulphates is evaporated to a small volume, and the minute quantity of magnesium which

it contains is precipitated as ammonium-magnesium phosphate. The sulphates of the alkaline earths are converted into carbonates by fusion with potassium-sodium carbonate, and the metals are separated and determined by the methods of Fresenius.

The filtrate from the carbonates contains, besides the greater portion of the magnesium, weighable quantities of barium and calcium — more of the former than of the latter. It is treated with 3 or 4 drops of dilute sulphuric acid, and afterwards with a quantity of ammonium oxalate sufficient to convert all of the magnesium into oxalate. The precipitate contains the barium as sulphate, the calcium as oxalate, and it may contain a small amount of magnesium oxalate. After standing for 12 hours in a moderately warm place, it is collected upon a small filter, washed, and treated with dilute hydrochloric acid. The barium sulphate remaining on the filter is determined in the usual manner. The filtrate is neutralized with ammonia and treated with a very little ammonium oxalate. The reprecipitated calcium oxalate is free from magnesium. The filtrate is added to that from the first precipitation of oxalate. The solution containing the magnesium — except that recovered from the carbonates of the alkaline earths — is evaporated to dryness in a platinum dish, and the ammonium salts are volatilized. The residue is dissolved in a little dilute hydrochloric acid and the magnesium precipitated as ammonium-magnesium phosphate.

THE ANALYSIS OF A SOLUTION CONTAINING THE ALKALIES, ALKALINE EARTHS, AND MAGNESIUM

The separation and determination of potassium, sodium, calcium, and magnesium is a frequently recurring problem in mineral analysis. With the calcium in minerals there is often associated more or less strontium and — more rarely — a small quantity of barium. The procedure here recommended provides for the isolation and estimation of all of the metals in question.

It may, of course, be somewhat simplified if one or more of them, e.g. barium or strontium or both barium and strontium, are known to be absent.

1. The Preliminary Treatment. The solution, owing to earlier treatment which it would be premature to describe in this place, will be free from phosphoric acid and from any other acid which might, under certain conditions, precipitate one or more of the metals. It will, however, in consequence of the previous separation of iron, aluminium, etc., usually contain considerable quantities of ammonium salts, which should be removed before proceeding to the separation. To this end, the solution is evaporated to dryness in a platinum dish and the ammonium salts are cautiously volatilized. The residue is dissolved in water with the aid of a little hydrochloric acid, and the solution considerably diluted.

2. Separation of the Alkaline Earths from Magnesium and the Alkalies. The process is essentially the same as for the separation of the alkaline earths from magnesium. The solution—prepared as described under 1—will be acid. It is treated with ammonia until the reaction becomes alkaline. If a precipitate appears, hydrochloric acid is cautiously added until it is dissolved, and the solution is again made alkaline with ammonia. This treatment is repeated until there is formed a quantity of ammonium chloride sufficient to prevent the precipitation of magnesium by ammonia. The solution is then treated with more ammonia and finally with a slight excess of ammonium carbonate. The beaker in which the precipitation was made is covered and allowed to stand for an hour in a warm place. The precipitate is collected and washed with water to which has been added a very little ammonia.

The precipitate will probably contain a small quantity of ammonium-magnesium carbonate, while the filtrate will contain some calcium and a large quantity of barium, if that element is present in the material under investigation. The presence of strontium in the filtrate is hardly to be feared, owing

to the very slight solvent action of ammonium chloride on strontium carbonate. The precipitate and the filtrate must, therefore, be worked over—the former for the recovery of magnesium and the latter for the recovery of calcium, or for the recovery of both calcium and barium. The exact procedure to be adopted will, in both cases, depend upon the presence or absence of other alkaline earths than calcium.

The Precipitate

If, as happens in the majority of cases, calcium is the only alkaline earth to be considered, the precipitate is dissolved in hydrochloric acid. The dilute acid solution is made distinctly alkaline with ammonia. If a precipitate appears, it is dissolved in hydrochloric acid and the solution is again made alkaline with ammonia. A moderate excess of ammonium oxalate is then added. After 12 hours the calcium oxalate is collected and washed in the usual manner. It will probably be sufficiently free from magnesium, but in case exact results are required, the oxalate may be dissolved in hydrochloric acid and the calcium reprecipitated by the addition of ammonia and a little ammonium oxalate. The filtrate or filtrates containing the small quantity of magnesium recovered from the calcium carbonate are acidified with hydrochloric acid, evaporated to a small volume, and added to the first filtrate, which contains the greater part of the magnesium.

If the material under investigation contains, besides calcium, barium or strontium, or both barium and strontium, the precipitate of carbonates is dissolved in hydrochloric acid and the solution is treated with dilute sulphuric acid and then with half its volume of alcohol. After standing for 12 hours the precipitate is collected upon a filter and washed with a mixture of 1 part of alcohol and 2 parts of water. The filtrate contains the magnesium which was precipitated with the carbonates of the alkaline earths, and also the portion of the calcium not

precipitated by the sulphuric acid. To remove the latter, the alcohol is evaporated and the solution is made alkaline with ammonia and treated with ammonium oxalate, etc., as directed above. By this treatment the alkaline earths will be freed from magnesium, but they will be left partly in the form of sulphates and partly in the form of oxalate. Both the sulphates and the oxalate must, however, be converted into carbonates before the metals can be separated. To this end the oxalate is heated in a platinum crucible to convert it into carbonate. The sulphates are brought into the same crucible with the calcium carbonate and mixed with sodium-potassium carbonate. The mixture is fused and treated with water. The insoluble carbonates are collected upon a filter and washed until they are free from the sulphates of the alkalis. Finally, the alkaline earths are separated and determined, as prescribed in Exercise XLIX. The filtrate containing the small quantity of magnesium extracted from the carbonates of the alkaline earths should not, when barium or strontium is present, be incorporated with that which contains the greater portion of the magnesium. It is rather to be evaporated to dryness and heated to expel ammonium salts, after which the residue is to be dissolved and the magnesium precipitated as ammonium-magnesium phosphate.

In order to avoid a needless multiplication of processes, the isolation and determination of the individual alkaline earths, after the removal of the magnesium precipitated with them by ammonium carbonate, should be postponed until the alkaline earths in the filtrate have been recovered.

The Filtrate

The filtrate from the carbonates of the alkaline earths contains the alkalis, the magnesium, — except a small quantity which is separately determined when barium or strontium is associated with the calcium, — some calcium, and possibly also barium. The first step to be taken is for the recovery of the calcium,

or for the recovery of calcium and barium, if the latter element is present.

If barium is absent, the solution will contain all of the magnesium and some oxalic acid, since in that case the magnesium recovered from the precipitate of calcium carbonate is added to the filtrate. It is made alkaline with ammonia and treated with a quantity of ammonium oxalate which is certainly somewhat more than equivalent not only to the calcium but also to the magnesium. The necessity for this precaution is due to the solubility of calcium oxalate in solutions containing magnesium chloride. After 12 hours the precipitate of calcium oxalate is collected and washed in the usual manner. It contains some magnesium oxalate. It is therefore dissolved in hydrochloric acid, and the calcium is reprecipitated by the addition of ammonia and a little ammonium oxalate. After standing for 12 hours the precipitate, which is now free from magnesium, is collected, washed, and converted into carbonate, either separately or with the main body of calcium oxalate. The filtrate is added to that which contains the alkalies and the greater portion of the magnesium.

If the material under examination contains barium, the procedure is as follows: The filtrate is treated first with 3 or 4 drops of dilute sulphuric acid and then with ammonium oxalate as described above. After 12 hours the precipitate is collected, washed, and treated on the filter with hydrochloric acid. The barium sulphate remains as an insoluble residue, while the calcium oxalate and the little magnesium oxalate which was precipitated with it are dissolved. The solution is made alkaline with ammonia and treated with a small quantity of ammonium oxalate. The reprecipitated calcium oxalate is free from magnesium, and the filtrate from it is added to that which contains the alkalies and the greater portion of the magnesium. The barium and the calcium thus recovered—the former as sulphate and the latter as oxalate—can, of course, be dealt with separately, or be added to and worked over with the main body of the alkaline earths.

3. Separation of Magnesium from the Alkalies. After the removal of the alkaline earths in the manner previously described, the solution contains the alkalies, nearly all of the magnesium, — all of it when calcium is the only alkaline earth to be determined, — and considerable quantities of ammonium salts. The acids which are represented in the solutions by their salts are hydrochloric, oxalic, and sulphuric. The last of these, sulphuric acid, can be present only when barium is one of the constituents to be estimated, and even then only in small quantity. The first step to be taken has for its object the removal of the ammonium salts in such a manner as to leave the alkalies and the magnesium in the form of chlorides. The solution is acidified with hydrochloric acid and evaporated to dryness in a platinum dish. The residue is then cautiously ignited to expel the ammonium compounds. Owing to the presence of oxalates, a portion of the alkalies may, during the ignition, be converted into carbonates; hence the material is repeatedly treated with small quantities of ammonium chloride and reheated. This course will also make more certain the removal of the last traces of sulphuric acid. The chlorides are dissolved in water and the magnesium is separated and determined as oxide by the mercuric oxide method. Finally, the alkalies are isolated and weighed as chlorides and afterwards separated by means of platinum chloride.

THE HARDNESS OF WATER

The so-called “hardness” of water is due to the presence in it of soluble salts of calcium and magnesium. These react with the oleates, palmitates, and stearates of the alkalies, of which soaps are largely made up, forming insoluble oleates, palmitates, and stearates of calcium and magnesium. Hence the proper action of soap upon fatty substances cannot be secured until all of the calcium and magnesium in a water have been precipitated. The soluble salts of barium and strontium behave

towards soap in the same manner as those of calcium and magnesium; the fact is, however, of little significance, owing to the very rare occurrence of these metals in natural waters.

The hardness of water is of two kinds,—“temporary” (that which disappears when the water is boiled) and “permanent” (that which is not affected by boiling). The temporary hardness is due to the presence of the acid carbonates of calcium and magnesium which are decomposed by heat with deposition of the neutral insoluble carbonates, while the permanent hardness is caused by those salts, mainly chlorides and sulphates, whose composition is not changed in boiling aqueous solutions.

It is customary to estimate the hardness of a water by means of a standard alcoholic solution of soap rather than by a quantitative determination of the calcium and magnesium which it contains. The soap solution is standardized by means of a solution of calcium chloride of known concentration.

There is as yet no satisfactory uniformity of practice as regards the statement of results. In other words, the so-called “degree” of hardness has a different significance in different countries and sometimes within the limits of the same country. In France, and usually in England and America, a milligram of calcium carbonate and 100 cc. of water are made the basis of computation; while in Germany the same weight of calcium oxide and an equal volume of water are made the units. In the former countries a water is said to have 1, 2, 3, etc., degrees of hardness when 100 cc. of it will destroy as much soap as 1, 2, 3, etc., milligrams of calcium carbonate dissolved in the same volume of water. The German “degrees of hardness” are, of course, related to those of the first-named countries inversely as the molecular weights of CaO and CaCO_3 , or directly as 99.34 to 55.68. In England and America there are also used, to some extent, the *gallon* as the unit measure of the water, and the *grain* as the unit weight of the calcium carbonate. The English or “imperial” gallon of water weighs 70,000 grains, while 100 cc. of water weighs 100,000 milligrams; hence degrees of

hardness calculated on the basis of the imperial gallon and the grain are related to those calculated by the usual standard as 10 to 7. The United States gallon of water weighs approximately 58319 grains; hence degrees of hardness calculated on the basis of the U. S. gallon and the grain are related to those calculated by the usual standards as 10 to 5.8319. The following table gives the numbers by which degrees of hardness of any one kind are to be multiplied in order to convert them into the equivalent number of degrees of other kinds.

To Convert

Degrees French, Eng., and Am. into degrees German . .	0.560
Degrees German into degrees French, Eng., and Am. . .	1.786
Grains per imperial gallon into milligrams per 100 cc. . .	1.429
Milligrams per 100 cc. into grains per imperial gallon . .	0.700
Grains per U.S. gallon into milligrams per 100 cc. . .	1.715
Milligrams per 100 cc. into grains per U.S. gallon . . .	0.583
Grains per imperial gallon into grains per U.S. gallon . .	0.833
Grains per U.S. gallon into grains per imperial gallon . .	1.200

EXERCISE L

DETERMINATION OF THE HARDNESS OF WATER

There are required :

1. A standard solution of calcium chloride. Weigh into a platinum or porcelain dish 1 gram of pure calcium carbonate. Treat with hydrochloric acid and cover the dish with a watch glass. When the material is dissolved, wash the under side of the cover back into the dish and evaporate the solution to dryness. Moisten the residue with distilled water and again evaporate, repeating the operation until the excess of the hydrochloric acid has been expelled. Dissolve the neutral residue in water and dilute to 1 liter.

2. A standard solution of soap. Rub together in a porcelain mortar 15 parts of lead plaster (*emplastrum plumbi*) and 4 parts by weight of pure dry potassium carbonate until a homogeneous

mass is obtained. Add strong alcohol, mix well, and then allow the insoluble matter to settle. Filter, and wash the lead carbonate with alcohol. Let the filtrate stand for a few hours, filter again if necessary, distill off the alcohol, and dry the soap residue upon the water bath.

Dissolve 10 grams of the soap in half a liter of 56 per cent alcohol, and proceed to standardize the solution in the following manner.

Measure 10 cc. of the standard calcium chloride solution into a glass-stoppered bottle or cylinder having a capacity of 200 or 250 cc., and dilute with recently boiled distilled water to a volume of 50 cc. Add the soap solution from a burette, 1 cc. at a time, shaking vigorously after each addition until evidences of a tendency to form a lather are observed. Afterwards proceed more cautiously, adding smaller quantities of the soap and placing the vessel on its side after agitating its contents until a lather is obtained which persists not less than 5 minutes. Repeat the experiment until a series of concordant results have been obtained, taking care, however, never to add more than 1 cc. of the soap solution at a time, even though the total volume which will be required is approximately known.

Having found the relation of the soap solution to that of the calcium chloride, dilute the former by stages with a mixture of 1 part of water and 2 parts of alcohol until 14.25 cc. of the soap are exactly equivalent to 10 cc. of the calcium chloride solution when the latter is diluted with distilled water to a volume of 50 cc.

In the place of the soap prepared as directed above, a good quality of Castile or of shaving soap may be used whenever the stability of the standard solution is of no consequence.

1. DETERMINATION OF TOTAL HARDNESS

Measure 50 cc. of tap water into the vessel used in standardizing the soap solution. Agitate for a few moments and then suck out the air above the water through a glass tube. Titrate

with the soap solution in exactly the same manner as when determining its strength by means of the standard solution of calcium chloride. The hardness of the water corresponding to the volume of the soap consumed will be found in the accompanying table.

If more than 16 cc. of the soap solution are required to produce a lather of the requisite permanence in 50 cc. of a water, a measured portion of the latter, e.g. 25 cc., should be diluted with distilled water to 50 cc. and the determination repeated. The degree of hardness as found in the table is then, of course, to be multiplied by a number corresponding to the dilution.

If the hardness of a water is largely due to magnesium salts, — a condition which is made apparent by the characteristic lightness of the curd, — the water should be diluted until not more than 7 cc. of the soap are required to produce a lather. Such waters, moreover, should be tested, after having stood for half an hour or longer, with reference to their power to reproduce the lather when agitated.

2. DETERMINATION OF PERMANENT HARDNESS

Gently boil a measured quantity of tap water in an open vessel, and when it has cooled, dilute to the original volume with recently boiled distilled water. Determine the hardness in the same manner as before.

The temporary hardness is the difference between the total and the permanent hardness.

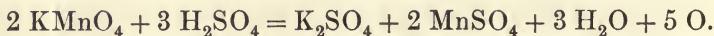
Table of Hardness, or Parts of CaCO_3 per 100,000 Parts of Water. Quantity of Water used, 50 cc.

Cc. of Soap Sol.	CaCO_3 per 100,000	Cc. of Soap Sol.	CaCO_3 per 100,000	Cc. of Soap Sol.	CaCO_3 per 100,000	Cc. of Soap Sol.	CaCO_3 per 100,000	Cc. of Soap Sol.	CaCO_3 per 100,000	Cc. of Soap Sol.	CaCO_3 per 100,000
.7	.00	3.3	3.64	5.9	7.29	8.5	11.05	11.1	15.00	13.7	19.13
.8	.16	.4	.77	6.0	.43	.6	.20	.2	.16	.8	.29
.9	.32	.5	.90	.1	.57	.7	.35	.3	.32	.9	.44
1.0	.48	.6	4.03	.2	.71	.8	.50	.4	.48	14.0	.60
.1	.63	.7	.16	.3	.86	.9	.65	.5	.63	.1	.76
.2	.79	.8	.29	.4	8.00	9.0	.80	.6	.79	.2	.92
.3	.95	.9	.43	.5	.14	.1	.95	.7	.95	.3	20.08
.4	1.11	4.0	.57	.6	.29	.2	12.11	.8	16.11	.4	.24
.5	.27	.1	.71	.7	.43	.3	.26	.9	.27	.5	.40
.6	.43	.2	.86	.8	.57	.4	.41	12.0	.43	.6	.56
.7	.56	.3	5.00	.9	.71	.5	.56	.1	.59	.7	.71
.8	.69	.4	.14	7.0	.86	.6	.71	.2	.75	.8	.87
.9	.82	.5	.29	.1	9.00	.7	.86	.3	.90	.9	21.03
2.0	.95	.6	.43	.2	.14	.8	13.01	.4	17.06	15.0	.19
.1	2.08	.7	.57	.3	.29	.9	.16	.5	.22	.1	.35
.2	.21	.8	.71	.4	.43	10.0	.31	.6	.38	.2	.51
.3	.34	.9	.86	.5	.57	.1	.46	.7	.54	.3	.68
.4	.47	5.0	6.00	.6	.71	.2	.61	.8	.70	.4	.85
.5	.60	.1	.14	.7	.86	.3	.76	.9	.86	.5	22.02
.6	.73	.2	.29	.8	10.00	.4	.91	13.0	18.02	.6	.18
.7	.86	.3	.43	.9	.15	.5	14.06	.1	.17	.7	.35
.8	.99	.4	.57	8.0	.30	.6	.21	.2	.33	.8	.52
.9	3.12	.5	.71	.1	.45	.7	.37	.3	.49	.9	.69
3.0	.25	.6	.86	.2	.60	.8	.52	.4	.65	16.0	.86
.1	.38	.7	7.00	.3	.75	.9	.68	.5	.81		
.2	.51	.8	.14	.4	.90	11.0	.84	.6	.97		

CHAPTER XX

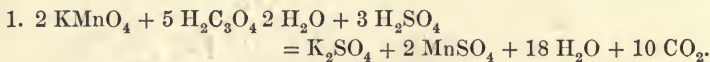
POTASSIUM PERMANGANATE

In the presence of oxidizable substances potassium permanganate is reduced. If the solutions to which it is added are acid, the reduction is generally complete in accordance with the following equation :



In other words, each molecule of potassium permanganate in acid solutions usually yields $2\frac{1}{2}$ atoms of oxygen which are available for oxidizing purposes. If, on the other hand, the solutions are neutral or alkaline, the reduction is incomplete and not always uniform in extent. The manganese of the permanganate is, in such cases, precipitated in the form of an oxide which contains relatively more oxygen than MnO and which may have the composition represented by MnO_2 .

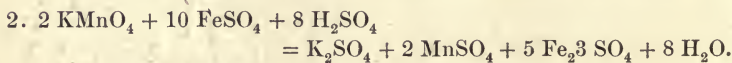
The following equations represent some of the more important of those reactions of potassium permanganate which are employed for the quantitative determination of oxidizable substances.



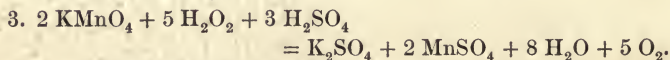
1 molecule $\text{KMnO}_4 = 2\frac{1}{2}$ molecules of oxalic acid.

1 molecule $\text{KMnO}_4 = 2\frac{1}{2}$ molecules of an acid oxalate.

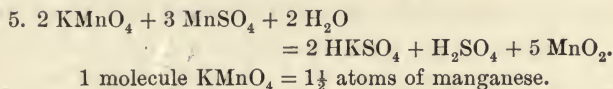
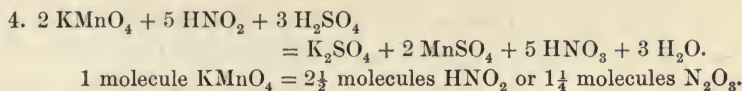
1 molecule $\text{KMnO}_4 = 1\frac{1}{4}$ molecules of potassium tetroxalate.



1 molecule $\text{KMnO}_4 = 5$ atoms of ferrous iron.



1 molecule $\text{KMnO}_4 = 2\frac{1}{2}$ molecules of H_2O_2 .



Atomic Weights

Oxygen	15.88	Sulphur	31.83
Carbon	11.9	Nitrogen	13.93
Potassium	38.82	Manganese	54.6
Iron	55.5		

Molecular Weights and Equivalent Numbers

Potassium permanganate	156.94	Equivalent number	156.94
Oxalic acid	125.08	" "	312.7
Acid potassium oxalate	127.14	" "	317.85
Potassium tetroxalate	252.22	" "	315.28
Ferrous ammonium sulphate	389.34	" "	1946.7
Hydrogen peroxide	33.76	" "	84.4
Nitrous acid anhydride	75.5	" "	94.38
Ferrous oxide	71.38	" "	356.9
Metallic iron	55.5	" "	277.5
Ferric oxide	158.64	" "	396.6
Manganese	54.6	" "	81.9
Manganous oxide	70.48	" "	105.72

The weight of 1 cc. of oxygen, latitude 45° , sea level, temperature 0° , pressure 760 mm., is 0.001429908 gram.

The table on page 457 is designed to facilitate the computation of analytical results. It contains the substances more commonly determined by potassium permanganate, and gives, for any unit quantity of each, the equivalent quantities of the others.

Three examples will sufficiently illustrate the method of using the table.

1. Suppose it is required to find how much potassium tetroxalate is equivalent, in reducing power, to 100 milligrams of ferrous oxide. The salt will be found to be No. IV in the column giving the composition of the substances; and by following column IV down to the horizontal line on which the equivalents of ferrous oxide are given, the number 0.88338 will be found. This, multiplied by the weight of the ferrous oxide, will give the equivalent weight of potassium tetroxalate, i.e. 88.338 milligrams.

2. Suppose it is required to find how much ferrous oxide 100 cc. of oxygen, under standard conditions, will convert into ferric oxide. By following column VI down to the line of oxygen volume-equivalents, the number 0.0128473149 will be found, and this multiplied by 100 will give the weight of ferrous oxide which 100 cc. of oxygen will convert into ferric oxide, i.e. 1.28473 grams.

3. In the same way, by following down columns XIII and XIV to VI, 11.214 milligrams and 7.784 cc. would be found to be the weight and volume respectively of the oxygen required to convert 100 milligrams of FeO into Fe_2O_3 .

The substances which are ordinarily employed to determine the strength of potassium permanganate solutions are oxalic acid, acid potassium oxalate, potassium tetroxalate, ferrous ammonium sulphate, and metallic iron in the form of wire. Other substances not so frequently used for this purpose are sodium oxalate, lead oxalate, ferric ammonium sulphate reduced by metallic zinc, manganous sulphate, and acidified solutions of potassium iodide from which potassium permanganate liberates an equivalent quantity of iodine.

1. Oxalic Acid

The preparation of oxalic acid entirely free from acid oxalates of the alkalis is a matter of some difficulty. Simple recrystallization from cooling saturated solutions does not suffice owing

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
I. KMnO_4	1.0000	1.99248	2.02529	2.00892	1.76819	2.27412	12.40410	2.52708	0.53779	0.60138	0.52186	0.67363	0.25296	177.00898
II. $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	0.50180	1.00000	1.01647	1.00825	0.88743	1.14135	6.22546	1.26831	0.26091	0.30182	0.26191	0.33800	0.12696	88.84037
III. HKC_2O_4	0.49375	0.99380	1.00000	0.99191	0.87305	1.12286	6.12459	1.24776	0.26553	0.29693	0.25767	0.33261	0.12490	87.39889
IV. $\left\{ \begin{array}{l} \text{HKC}_2\text{O}_4 \\ \text{H}_2\text{C}_2\text{O}_4 \end{array} \right\} 2\text{H}_2\text{O}$	0.49778	0.99182	1.00815	1.00000	0.88017	1.13201	6.17451	1.25793	0.26770	0.29935	0.25977	0.33532	0.12592	88.11264
V. Fe	0.56355	1.12685	1.14541	1.13614	1.00000	1.28613	7.01514	1.42919	0.30414	0.34011	0.29514	0.38097	0.14306	100.10636
VI. FeO	0.43973	0.87616	0.89059	0.88338	0.77753	1.00000	5.45447	1.11124	0.23648	0.26444	0.22948	0.29622	0.11124	77.84029
VII. $\left\{ \begin{array}{l} \text{FeSO}_4 \\ (\text{NH}_4)_2\text{SO}_4 \end{array} \right\} 6\text{H}_2\text{O}$	0.08062	0.16063	0.16328	0.16196	0.14255	0.18534	1.00000	0.20373	0.04336	0.04848	0.04297	0.05431	0.02039	14.26792
VIII. Fe_2O_3	0.39571	0.78845	0.80144	0.79496	0.69970	0.89990	4.90847	1.00000	0.21281	0.23797	0.20651	0.26657	0.10010	70.05206
IX. H_2O_2	1.85948	3.70498	3.76900	3.73555	3.28791	4.22867	23.06517	4.03905	1.00000	1.11825	0.97038	1.25261	0.47038	329.14882
X. N_2O_3	1.60285	3.31320	3.35777	3.34054	2.94024	3.78152	20.62619	4.20216	0.89426	1.00000	0.86777	1.12015	0.42064	294.35021
XI. Mn	1.91624	3.81807	3.88095	3.84937	3.38628	4.35775	23.76923	4.84249	1.03053	1.15238	1.00000	1.29084	0.48474	339.19725
XII. MnO	1.48449	2.95781	3.00653	2.98222	2.62486	3.37590	18.41373	3.75142	0.79833	0.89274	0.77469	1.00000	0.37552	262.77045
XIII. O_2 (weight)	3.95315	7.87657	8.00630	7.94156	6.98990	8.98990	49.03556	9.98992	2.12594	2.37733	2.06297	2.66297	1.00000	699.75082
XIV. O_2 (volume)	0.00564	0.01125	0.01143	0.01134	0.00998	0.01284	0.07007	0.01427	0.00303	0.00339	0.00294	0.00380	0.00142	1.00000
	99676	62487	98426	91246	91263	73149	53094	63949	81383	73948	81492	55972	908	

to the difficult solubility of such oxalates in cold water and their ready solubility in hot water. Since, however, the molecular weights of the acid oxalates of the alkalis do not differ greatly from the molecular weight of oxalic acid with its two molecules of water of crystallization, the entire removal of the former is not necessary. An acid sufficiently pure for the standardization of potassium permanganate may be prepared by saturating cold water with the commercial acid and evaporating to crystallization. This process, two or three times repeated, gives a product which yields but little residue on ignition. A still purer acid is obtained by recrystallizing, first from hot dilute hydrochloric acid (10 to 15 per cent), then from hot alcohol, and finally from water. The aqueous solution must be heated until the odor of ethyl oxalate disappears. The purest oxalic acid is prepared by dissolving in a mixture of equal parts of alcohol (95 per cent) and ether. The solution is filtered, diluted with water, freed from the ether and a portion of the alcohol by distillation, and then evaporated on the water bath to the crystallizing point. If the acid thus obtained has the odor of ethyl oxalate, it must be again dissolved in water and recrystallized.

Oxalic acid is stable at ordinary temperatures in an atmosphere containing the usual amount of moisture. It cannot, however, be dried, either in a desiccator or in a hot-air bath. At ordinary temperatures potassium permanganate—even in the presence of sulphuric acid—acts very slowly upon oxalic acid. The presence of manganous salts greatly facilitates the reaction. In practice it is customary to hasten the reduction of the permanganate by heating the solution of oxalic acid to 60° or 65° . Once well started, the reaction—owing to the accumulation of manganous sulphate in the solution—proceeds rapidly even though the temperature of the solution falls nearly to that of the surrounding air.

2. Potassium Tetroxalate

This salt is usually preferred to oxalic acid for the standardization of potassium permanganate. Its preparation has already been described. Like oxalic acid, it is stable in the air at ordinary temperatures, but cannot be dried in a desiccator or in a hot-air bath.

3. Ferrous Ammonium Sulphate

The salt is dissolved in cold water and precipitated by alcohol. The precipitate, which should be entirely free from any yellow color, is collected upon a filter and washed with alcohol. Ferrous ammonium sulphate suffers some oxidation in contact with the air, and should, therefore, be freshly prepared.

EXERCISE LI

DETERMINATION OF IRON BY MEANS OF POTASSIUM PERMANGANATE

I. PREPARATION OF THE PERMANGANATE SOLUTION

Dissolve about 3.3 grams of potassium permanganate in water. Filter the solution through asbestos and dilute the filtrate to 1 liter. Weigh into beaker glasses two portions (from 0.100 to 0.150 gram each) of pure potassium tetroxalate. Dissolve in water, heat to about 60°, add 2 or 3 cc. of dilute sulphuric acid, and titrate to a barely perceptible rose color with the permanganate solution. Calculate from the results the amount of permanganate in each cubic centimeter of the solution. Divide 2.82775, the number of grams required for 1 liter, by the quantity contained in 1 cc., and thus find how many cubic centimeters must be diluted to a liter. Each cubic centimeter of a solution of permanganate prepared in this manner is equivalent to 5 milligrams of iron.

Verify the strength of the standard solution by titrating it against weighed quantities of potassium tetroxalate and also of freshly prepared ferrous ammonium sulphate. Finally, test the solution again in the following manner: Measure out 25 cc. of the permanganate solution, add a measured quantity of a standard solution of sulphuric acid which will more than suffice to neutralize the metals in the permanganate, and then reduce with the least possible amount of neutral hydrogen superoxide. Determine the excess of the sulphuric acid with a dilute standard solution of ammonia, using litmus as the indicator. The reaction involves the neutralization of $1\frac{1}{2}$ molecules of sulphuric acid for each molecule of potassium permanganate. Commercial hydrogen superoxide may be brought to a neutral condition by agitating it with ignited zinc oxide and then filtering through asbestos.

It will be seen that having a solution of potassium permanganate of known strength, one may readily standardize a solution of sulphuric acid by the same method.

Solutions of permanganate are not wholly stable. The usual cause of their deterioration is the presence in them of the oxides of manganese. The salt in solution is decomposed by these oxides, which are often mingled with it in the dry state, or which form when the solutions are allowed to stand for some time. The decomposition is attended by the evolution of oxygen, and a small quantity of the oxide will decompose an unlimited amount of the permanganate, though the rate of the decomposition increases rapidly with the quantity of the oxide. The rate of the decomposition is also affected by the temperature and by the light. All solutions of permanganate should therefore be filtered through asbestos when made, and those which have been made for some time should be refiltered into clean bottles. Moreover, a solution which has been exposed in a burette should be filtered before returning it to the bottle from which it was taken.

In all quantitative determinations which involve a complete reduction of potassium permanganate, the solutions of the

substances to be determined must be sufficiently acidified with sulphuric acid. If an insufficient quantity of the acid is used, the solutions become brown and turbid in consequence of the precipitation of manganese oxides, and the reduction is incomplete. The slight rose color which is imparted to the solution by a small excess of permanganate, and which is relied upon to indicate the completion of the reaction, soon disappears owing to the action of permanganate on manganous salts. This oxidation of the manganese in manganous salts is slow, however, under ordinary conditions, and does not take place in the presence of more easily oxidized matter; hence manganous salts do not interfere with the use of permanganate in the determination of iron, oxalic acid, etc.

The presence of hydrochloric acid and of chlorides is to be avoided if possible. They reduce the permanganate with liberation of chlorine, but the irregularities due to this reaction may be avoided by adding manganous sulphate to the solution. The difficulty may also be overcome to a great extent by largely diluting the solution of the substance to be determined.

II. DETERMINATION OF METALLIC IRON

The "Bunsen valve" which is required for this experiment is made by slipping a piece of small, black, rather thick rubber tubing, 50 or 60 mm. long, over a round wooden rod, and cutting in the middle of it a short longitudinal slit. The rod should not be so large as to stretch the rubber to any great extent, and care should be taken that the tubing is not twisted on the rod when the slit is made. The knife should be wet and very sharp. One end of the tube is closed with a short glass rod, and the other is slipped over the end of a glass tube. The other end of the glass tube is passed through a perforated rubber stopper which fits a small flask in which the iron is to be dissolved. Neither the glass rod nor the tube should be pushed so far into the rubber as to stretch it in the vicinity

of the slit. Such an arrangement, if properly made, permits the gas which is generated within the flask to escape freely into the air, but closes effectually against any current in the other direction.

Dissolve from 100 to 150 milligrams of carefully cleansed piano wire in an excess of quite dilute sulphuric acid. The flask and its contents may be moderately heated to expedite the reaction. When the iron has dissolved, remove the flask from the bath and introduce a very small quantity of acid sodium carbonate which is free from iron. When the solution has cooled to 50° or 60° , open the flask again and introduce another small quantity of the carbonate. Titrate to color as soon as the evolution of carbon dioxide ceases.

If the specimen of wire is one which deposits carbon when dissolved in sulphuric acid, the experiment is better carried out in the following manner: The iron and the sulphuric acid are placed in a quarter-liter measuring flask which is connected with another small flask by means of a glass tube bent to two right angles. The tube is cut in the middle of the horizontal portion and again joined by means of a short piece of rubber tubing which may be closed by a Mohr pinchcock. The end towards the measuring flask passes through a rubber stopper and reaches to a point just above the mark on the neck, while the other end reaches nearly to the bottom of the second flask, in which has been placed a quantity of boiled distilled water. When the iron is dissolved the rubber tube is closed and the contents of the flasks are allowed to cool to the temperature of the air. The measuring flask is then filled to the mark by opening the pinchcock, and the contents are well shaken. Finally, when the carbon has subsided, measured portions of the liquid are withdrawn and titrated with permanganate.

III. CONFIRMATION OF THE RESULTS BY THE GRAVIMETRIC METHOD

Dissolve another portion of the wire (from 0.100 to 0.200 gram) in nitric acid in a covered porcelain dish. Wash anything which may have splattered upon the under side of the cover back into the dish. Evaporate the solution upon a water bath and moisten the residue with strong nitric acid. Evaporate again and heat the residue in a hot-air bath for an hour at 120°. Moisten the dried material with a few drops of strong nitric acid, add water, and heat for half an hour on the water bath. Filter, and wash the paper. Heat the filtrate and washings nearly to the boiling point and precipitate the iron with a small excess of ammonia. Add the ammonia slowly and stir the liquid constantly and vigorously during precipitation. Keep the vessel containing the precipitate hot for an hour or longer, and then set it aside for several hours. Filter, wash the precipitate with hot water, and partially dry the paper. While the paper is still somewhat moist roll it together and place it in a weighed porcelain crucible. Heat the crucible very cautiously until the paper is dry and begins to blacken. Burn it slowly and then moisten the mass with two or three drops of strong nitric acid. Evaporate the acid. Cover the crucible and carefully heat it until all tendency on the part of the oxide to decrepitate has passed. Remove the cover and heat the material exposed to the air for an hour over a Bunsen burner. Weigh, and again heat for half an hour in order to ascertain whether the weight is constant. Compare the weight of the iron in the oxide with that found by the volumetric method.

It is preferred by many to use iron wire in which the iron has been determined gravimetrically for the standardization of permanganate solutions. It is to be observed in regard to this practice that the carbon in the iron may give rise to errors.

Owing to the volatility of ferric chloride, ferric hydroxide which is precipitated from solutions containing chlorides must be washed until the filtrate is free from chlorine.

Iron in the ferrous condition may also be determined volumetrically by means of a standard solution of potassium dichromate. The solution of the ferrous salt is acidified with sulphuric acid and treated with the dichromate until a drop of the liquid taken out upon a glass rod and applied to a drop of a solution of potassium ferricyanide upon a white porcelain surface no longer gives a blue color.

The method gives good results in the presence of chlorides. The ferricyanide used to detect the completion of the reaction must, of course, be free from potassium ferrocyanide.

EXERCISE LII

DETERMINATION OF FERROUS AND FERRIC IRON IN A SILICATE

Prepare 2 or 3 grams of manganese dioxide by slowly stirring a dilute solution of manganese sulphate into a hot solution of potassium permanganate which contains more of the permanganate than is required for the oxidation of the manganese. Filter, wash the precipitate, and mix it with aqueous hydrofluoric acid in a platinum retort. After the acid has been in contact with the oxide for a few hours, slowly distill it into a platinum receiver which contains a little water and is kept cool by ice water. Dilute a little of the distillate in a platinum dish and ascertain whether it reduces permanganate. If it does, return the remainder of the acid to the retort and allow it to stand for a longer time in contact with the oxide.

The apparatus in which the silicate is to be decomposed consists of two glass funnels of equal size, the rims of which are held together by a broad rubber band. One of them is placed in a hot-water funnel and connected at its lower end with a carbon dioxide generator. The stem of the other is cut off at a point about 10 or 15 mm. from the conical part.

Place about half a gram of finely pulverized biotite in a small platinum dish and add to it 5 or 6 cc. of dilute sulphuric acid. Put the dish on a small triangle in the bottom of the lower funnel and conduct carbon dioxide through the apparatus until it is believed that the air has been displaced. Heat the water funnel and pour 10 or 15 cc. of the purified hydrofluoric acid down a stout platinum wire through the orifice in the upper funnel. Diminish the flow of carbon dioxide as much as is consistent with the protection of the contents of the dish from the air. Occasionally stir the decomposing silicate with the platinum wire and continue to heat until the decomposition appears to be complete. Transfer the dish to a beaker containing boiling water and add a little acid sodium carbonate. Remove the dish and rinse both it and the platinum wire into the beaker with hot water. Add a little more sodium carbonate and titrate with permanganate. Do not use the platinum wire as a stirring rod during the titration.

Wind a platinum wire spirally about a rod of zinc and insert the pair in the solution, leaving one end of the wire above the surface. Heat gently and stir until a drop of the liquid fails to impart a red color to a solution of ammonium sulphocyanate. Allow the solution to cool, adding from time to time small portions of sodium carbonate. When it is cold remove the zinc and rinse it back into the beaker. Titrate with permanganate. Repeat the reduction and titration in the same manner as before, adding more sulphuric acid if necessary.

The first operation gives the ferrous, and the second the total, iron in the silicate. The difference between the two is, of course, the iron which is in the ferric condition.

The zinc which is used in the reduction must be free from arsenic and antimony and also from metals whose salts reduce permanganate. It must likewise be free from lead, since that metal forms with zinc an alloy which dissolves very slowly and often becomes detached from the rod.

The solution must not be allowed to become neutral, since in that condition the iron is deposited in metallic form.

EXERCISE LIII

DETERMINATION AND SEPARATION OF IRON AND ALUMINIUM

1. Weigh out about 5 grams of ferric ammonium sulphate ($\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$), and about 10 grams of pure aluminium ammonium sulphate ($\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$). Dissolve the salts in water. Transfer the solution to a quarter-liter flask and fill to the mark with water. Measure 50 cc. of the solution into a beaker glass. Add water and dilute sulphuric acid. Reduce the ferric salt with zinc and platinum, as directed in the preceding exercise, and determine the iron with the standard solution of permanganate.

2. Measure another 50-cc. portion of the solution into a porcelain dish. Add water and about 10 cc. of dilute hydrochloric acid. Heat nearly to the boiling point and then slowly add ammonia, stirring constantly until the liquid is very faintly ammoniacal. Continue to heat for half an hour and then determine whether the liquid is still slightly alkaline. If it is not, make it so with the least possible quantity of ammonia. Decant the clear portion of the liquid through a paper filter. Add boiling water to the residue in the beaker. Allow the precipitate to subside and then decant again. Bring the precipitate upon the paper and wash two or three times with hot water. Dissolve the mixture of hydroxides in the filter with dilute hydrochloric acid. Wash the paper thoroughly, collecting the filtrate in the porcelain dish which was used for the precipitation. Heat the solution and precipitate as before with the slightest possible excess of ammonia. Collect the precipitate upon a filter and wash with hot water until the filtrate gives no reaction for chlorine. Proceed with the filter and its contents as directed under Exercise LI, taking all possible precautions to avoid any spattering of the oxides in the crucible. From the weight of the mixed oxides and the known weight of

the iron oxide, calculate the weight of the aluminium oxide. Fuse some acid potassium sulphate in a platinum crucible or dish, applying just enough heat to keep the salt in the molten condition. When the fused mass becomes perfectly tranquil, pour it into a cold platinum dish or upon a piece of platinum foil. Pulverize the potassium pyrosulphate and add 2 or 3 grams of the powder to the crucible containing the mixture of iron and aluminium oxides. Heat the crucible over a Bunsen burner until the oxides are completely dissolved in the fused pyrosulphate, keeping the temperature just high enough to produce a constant but very slow evolution of sulphur trioxide. Place the crucible when cold in a beaker. Add cold water, also a little dilute sulphuric acid, and stir until the fused sulphates are dissolved. Reduce with zinc and platinum and determine the iron by permanganate.

The iron in this mixture of oxides may also be determined by reducing in a current of dry hydrogen, dissolving the metallic iron in dilute sulphuric acid, and titrating with permanganate.

3. Place about 10 cc. of water in a large silver dish and add thin shavings of metallic sodium, one by one, until about 3 grams of the metal have been dissolved. Evaporate the excess of water quite rapidly. Fuse the residue and continue to heat until the molten hydroxide becomes tranquil. Place the dish under a bell jar until needed.

Measure 50 cc. of the solution of sulphates into a porcelain dish. Precipitate the iron and aluminium with a very slight excess of ammonia, as previously directed. Collect the precipitate upon a filter and wash it with hot water. Dry the filter at 100°. Open it over a piece of glazed paper and scrape off the precipitate. Burn the paper in a platinum wire and let the ash fall into a porcelain or platinum dish. Place the precipitate and ash on the center of the sodium hydroxide in the silver dish. Heat the dish cautiously until all tendency on the part of the contents to spatter ceases. Keep the hydroxide in the molten condition for about half an hour. Allow the dish and

its contents to cool. Add quickly and at one time about 300 cc. of water. Keep the solution hot for an hour in order to effect a complete separation of the iron. Decant through a filter and wash the precipitate several times by decantation, using hot water. Bring it upon the filter and wash with boiling water until the filtrate shows a neutral reaction. Dissolve the precipitate in hydrochloric acid. Reprecipitate with ammonia from the hot solution, and proceed as previously directed to obtain the weight of the ferric oxide.

Acidify the filtrate which contains the aluminium with nitric or hydrochloric acid. Precipitate from the hot solution with the least possible excess of ammonia. Filter, and wash with hot water. Dissolve the precipitate with hydrochloric acid. Precipitate again with ammonia. Filter, and wash with hot water until the filtrate gives no reaction for chlorine. Roll up the paper and precipitate and place the roll in a platinum crucible. Heat cautiously over a Bunsen burner until the paper is burned and the residue shows no inclination to decrepitate, and finally to constant weight over the blast lamp.

The reprecipitation of the iron and aluminium by ammonia is necessary in order to free the hydroxides from alkali.

EXERCISE LIV

DETERMINATION OF MANGANESE BY POTASSIUM PERMANGANATE

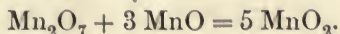
BY VOLHARD'S METHOD

Dissolve about 10 grams of manganese sulphate in a quarter liter of water and test the solution for iron. If no iron is found, dilute to half a liter. If iron is present, add 2 or 3 cc. of dilute nitric acid and boil. Take out about one-tenth of the solution and precipitate the manganese in it with ammonium carbonate to which ammonia has been added. Filter, wash the precipitate, and add it to the main solution of the sulphate.

Heat the solution to the boiling point, stirring it constantly. Filter, and dilute the filtrate to half a liter.

Dissolve in a quarter liter of water about 25 grams of zinc sulphate which does not reduce permanganate in solutions acidified with sulphuric acid. If a suitable specimen of the sulphate is not obtainable, heat to redness in a platinum dish, in a muffle, somewhat more than the requisite amount of commercial zinc oxide, and add it to a quantity of hot dilute sulphuric acid which is insufficient to dissolve the whole of the oxide. Filter, and dilute the filtrate so that each cubic centimeter of the solution shall contain about one-tenth of a gram of zinc sulphate.

Measure 10 cc. of the manganese sulphate solution into a three-quarter liter flask. Add 10 cc. of the zinc sulphate solution and 2 or 3 drops of dilute nitric acid. Dilute with water, which does not reduce permanganate, to about 250 or 300 cc. Heat to the boiling point and then add rapidly nearly as much standard potassium permanganate as it is thought will be required to precipitate the manganese according to the equation :



Shake the flask vigorously and then add more cautiously the remainder of the permanganate required to produce a permanent color, shaking the flask from time to time. If the solution is turbid and slow to clear in consequence of the fineness of the precipitate, it may be heated again, but not to the boiling point. Having found by the first experiment very nearly the amount of permanganate required, repeat the determination with another equal portion of the sulphate, adding at once, to within one- or two-tenths of a cubic centimeter, all of the permanganate which the previous experiment has shown to be necessary, and finishing the determination with greater caution than before.

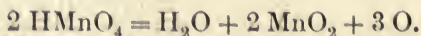
Test the constancy of the results by several repetitions of the experiment, using varying quantities of the manganese sulphate.

Proceed also in the following manner: Measure out a quantity of the sulphate solution and prepare it for the precipitation of the manganese as previously directed. Measure into another flask of sufficient size the quantity of permanganate which the previous work has shown to be required by the given volume of sulphate, and warm it upon the water bath. When the solution of the sulphate is boiling hot and that of the permanganate is warm, pour the former into the latter, rinsing the emptied flask with boiling water. During the transfer, the mixing of the liquids should be facilitated as much as possible by shaking and rotating the flask, and whenever the pouring is interrupted for this purpose, the flask containing the remainder of the sulphate should be again placed over the flame. It will be found that a further addition of permanganate is required in order to produce a permanent color.

REDUCTION OF PERMANGANIC ACID BY THE OXIDES OF MANGANESE

Measure 50 cc. of the standard permanganate solution into a flask and add to it the quantity of manganous sulphate which is required to reduce one-half of the permanganate to MnO_2 . Immerse the body of the flask in boiling water and heat until the color of the permanganate disappears, which may require from 2 to 3 hours. Now determine the remaining "active" oxygen by adding a measured but excessive quantity of a standard solution of oxalic acid or of tetroxalate, also a little sulphuric acid and titrating to color—when the manganese oxides have disappeared—with potassium permanganate.

It will be found that about three-tenths of the oxygen has disappeared, — in other words, that the excess of the permanganate has been reduced with the evolution of free oxygen by the oxide precipitated by the action of a portion of the permanganate on the manganous sulphate:



If the determination is made immediately after the disappearance of the color of the permanganate, the quantity of oxygen found will be very nearly that which would be obtained if all the manganese in the solution were in the dioxide condition. If the determination is postponed for any length of time, the quantity of oxygen found will be somewhat less.

EXERCISE LV 76

DETERMINATION OF MANGANESE AS PYROPHOSPHATE

BY GIBBS' METHOD

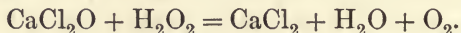
Acidify 20-cc. portions of the manganese sulphate solution used in the previous exercise with 3 or 4 cc. of dilute hydrochloric acid. Heat to the boiling point, and add a moderate excess of ammonium phosphate ($\text{H}(\text{NH}_4)_2\text{PO}_4$) in solution. Add ammonia, drop by drop, with constant stirring until a permanent precipitate forms. Stop adding the ammonia, but continue the stirring at the boiling temperature until the precipitate assumes a silky crystalline appearance. Add more ammonia, stirring vigorously after the addition of each drop, until all the manganese has been precipitated and the whole of the precipitate has become crystalline in appearance. Add a few more drops of ammonia. Place the beaker in ice water and let it remain there until the solution is perfectly cold. Filter through paper and wash the precipitate with a cold, faintly ammoniacal, 10 per cent solution of ammonium nitrate. The subsequent treatment of the precipitate is the same as in the determination of magnesium or phosphoric acid as magnesium pyrophosphate. Test the filtrate for manganese. The precipitate has the composition NH_4MnPO_4 , and like the corresponding magnesium salt, it is converted by heat into the pyrophosphate $\text{Mn}_2\text{P}_2\text{O}_7$.

EXERCISE LVI

DETERMINATION OF HYDROGEN PEROXIDE

If the solution of peroxide is concentrated, dilute 10 cc. of it to 100 cc. Measure off 10-cc. portions of the diluted solution, add water and dilute sulphuric acid, and titrate with permanganate. There are in use two ways of expressing the value of hydrogen peroxide solutions. One gives the percentage by weight, and the other the volume of free oxygen which a cubic centimeter of the solution would yield if the peroxide were decomposed into water and oxygen.

Another method (Lunge's) for the determination of hydrogen peroxide is based on the following reaction:



The free oxygen is determined by direct measurement or by absorption.

EXERCISE LVII

DETERMINATION OF NITROUS ACID

Weigh off about 5 grams of the commercial potassium nitrite, taking care to secure an average sample of the whole lot from which the material is taken. Dissolve in water and dilute to a liter. Measure 10-cc. portions into beakers. Add to each a measured but excessive quantity of permanganate, remembering that in the alkaline solutions only $1\frac{1}{2}$ atoms of oxygen per molecule of permanganate will be available for the oxidation of the nitrite. Warm for half an hour upon the water bath. In the meantime prepare a solution of oxalic acid whose strength is nearly equal to that of the permanganate. Add to the contents of each beaker the volume of oxalic acid which is equivalent to the volume of permanganate which was added to the nitrite. Acidify with sulphuric acid. When the solution has become clear and colorless, titrate to color with the

permanganate. The quantity of permanganate used in the last case is equivalent to the nitrite.

Measure off 10 cc. of the nitrite solution. Dilute with 300 cc. of water. Make the solution very slightly acid with sulphuric acid. Add permanganate until the nitrous acid is nearly all oxidized, then make the solution more strongly acid, and complete the titration. Owing to the limited solubility of nitric oxide in water, the solution of the nitrite must be very dilute, containing not more than 1 part of nitrous acid anhydride to 5000 parts of water. The end reaction is somewhat indefinite in consequence of the slowness with which nitric oxide is oxidized by permanganic acid.

Nitrogen dioxide may also be determined by permanganate. For this purpose a measured portion of the solution containing it, e.g. fuming nitric acid, is slowly stirred into a large quantity of cold water and the dilute solution titrated. Each molecule of the nitrous anhydride found is equivalent to four molecules of NO_2 , since $2 \text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_3 + \text{HNO}_2$.

CHAPTER XXI

THE ELECTROLYTIC DETERMINATION OF METALS

ELECTRICAL UNITS AND THEIR RELATIONS

1. THE AMPERE AND THE COULOMB

The *ampere* is the unit of the quantity of electricity flowing through a circuit. It is defined as the strength of the current which a unit of electromotive force (one volt) will cause to flow through a conductor whose resistance is unity (one ohm). It is also the quantity of current which, under certain conditions, will precipitate per second 0.3292 milligram of copper or 1.1172 milligrams of silver.

The *coulomb* is the quantity of electricity which flows through a circuit during one second when the strength of the current is one ampere.

The *ampere-hour* is the quantity of electricity which flows through a circuit during one hour when the strength of the current is one ampere. It is therefore equal to 3600 coulombs.

The current strength is the same in all parts of an undivided circuit.

2. THE OHM

The *ohm* is the unit of the resistance to the flow of a current in a conductor. It is equal to the resistance offered at 0° by a column of mercury whose length is 106.3 centimeters and whose cross section is equal to one square millimeter. The resistance of a conductor of any given material is directly proportional to its length and inversely proportional to the area of its cross section.

The *specific resistance* of a substance is the resistance found in a conductor made from that material whose length is one centimeter and whose cross section has an area of one square centimeter.

The resistance of any conductor is equal to the specific resistance of the material of which it is made multiplied by its length and divided by the area of its cross section :

$$R = \frac{\text{specific resistance} \times \text{length}}{\text{area of cross section}}.$$

With rising temperature the specific resistance of metals increases, while that of carbon, liquids, and generally of solutions, diminishes. The specific resistance of solutions also varies with concentration.

The *conductivity* of a material is the reciprocal of its resistance.

If a current is given two or more paths between two points in a circuit, it will distribute itself among them in quantities which are inversely proportional to the resistance or directly proportional to the conductivity of the several conductors, and the total conductivity of the divided line will be the sum of the conductivities of the individual lines. If, for example, the resistances of three parallel lines are 10, 20, and 30 ohms respectively, their separate conductivities will be $\frac{1}{10}$, $\frac{1}{20}$, and $\frac{1}{30}$, and the total conductivity will be $\frac{11}{60}$, or 0.18333; while the resistance of the lines, taken together, will be $\frac{1}{0.18333}$, or 5.45 ohms.

3. THE VOLT

The *volt* is the unit of electromotive force. It is the electrical pressure which will send one ampere of current through a conductor whose resistance is one ohm.

4. OHM'S LAW

Ohm's law of the current is expressed by the following equation :

$$C = \frac{E}{R};$$

in which

C represents the current in amperes,

E , the electromotive force in volts, and

R , the resistance of the circuit in ohms.

It will be seen that if any two of these values are known, the third can be calculated, for

$$E = CR \text{ and } R = \frac{E}{C}.$$

Determination of the Strength of the Current

The strength of the current is ascertained by measuring either its chemical or its electro-magnetic effects.

Instruments for the former purpose are known as voltameters, and these are classified as gas (oxy-hydrogen or hydrogen), or as weight voltameters, according as the gas resulting from an electrolysis of definite duration is measured, or the metal deposited on an electrode is weighed. The quantity of gas which is liberated per second in the oxy-hydrogen voltameter and the weight of metal which is precipitated in the silver or copper voltameter in the same unit of time have, for fixed conditions, perfectly definite equivalents in coulombs of current; hence, by noting the time of an electrolysis and measuring or weighing the products, the strength of the current can be ascertained. But voltameters are little used in the laboratory, owing principally to the long time required for a determination.

Instruments depending on the electro-magnetic effects of the current are likewise of two kinds. In one of these a magnet is displaced by the current flowing in its vicinity, while in the other a bar or needle of soft iron is employed which becomes a

magnet under the influence of the current and is then displaced. Instruments of the first kind are known as *galvanometers*, and of the second as *amperemeters* or *ammeters*. Only amperemeters are used in ordinary electrolytic work. These are provided with a scale for the direct reading of the amperage and often with two scales, one for small and the other for large currents. Amperemeters have a small resistance and are inserted in the circuit.

Determination of Voltage

The measurement of the fall or difference of potential between any two points in a circuit is usually made for practical purposes by means of a so-called voltmeter. This instrument resembles the amperemeter, but differs from the latter in that its resistance is so high that when it is inserted in a shunt between the two points, only a minute fraction of the current passes through the voltmeter; its employment does not, therefore, materially affect the conductivity of the line as a whole. An instrument measuring from 0 to 150 volts has a resistance of about 12,500 ohms. The range of the voltmeter is greatly enlarged by using "multipliers," i.e. standard resistances which are placed in series with it in the shunt circuit and thus increase the value of the scale divisions by definite multiples.

Having ascertained the quantity of the current flowing through the circuit, and the fall of potential between any two points on the same, the resistance in the line between them is found by the equation

$$R = \frac{E}{C}.$$

5. THE JOULE

The *joule* is the electrical unit of energy. It is equivalent to the quantity of heat developed in a circuit by one coulomb of a current whose electromotive force is one volt :

$$1 \text{ joule} = 1 \text{ coulomb} \times 1 \text{ volt.}$$

According to Joule's law, the heat in calories which is developed in a circuit with a resistance R , by a current C , in the time t , is expressed by the equation:

$$\text{calories} = C^2 R t \times 0.2381 = C R \times C t \times 0.2381.$$

But according to Ohm's law $C R = E$, the electromotive force of the current; hence

$$\text{calories} = E \times C t \times 0.2381.$$

If C is one ampere and t is one second, $C t$ is the coulomb; therefore

$$\text{calories} = E \times \text{coulombs (joules)} \times 0.2381.$$

$$\text{Joules} = \frac{\text{calories}}{0.2381}.$$

$$1 \text{ joule} = 0.2381 \text{ calorie.}$$

$$1 \text{ calorie} = 4.2 \text{ joules.}$$

6. THE WATT

The *watt* is the electrical unit of work. It is the mechanical equivalent of the joule.

Since the mechanical equivalent of the calorie is 3.0968 foot pounds per second, that of the joule ($= 0.2381$ calorie) is 0.73732 foot pound. The watt, therefore, is 0.73732 foot pound per second, and 745.94 watts equal 550 foot pounds per second, or one horse power.

The work, in watts, which can be accomplished by any current is the product of its quantity in amperes by its pressure in volts. Expressed in horse power, it is $\frac{Ec}{745.94}$. In the case of powerful currents, e.g. those of large dynamos, it is customary to employ the kilowatt ($= 1000$ watts $= 1.3406$ horse power) as the unit of work.

SOURCES OF CURRENT

The general employment of electricity for lighting, mechanical, and other purposes has brought the current in great abundance within the reach of nearly all laboratories. The current as it is obtained from the town supplies has, however, a far too high electromotive force for the ordinary electrolytic processes, and it must be transformed to a lower voltage. This is accomplished by means of dynamos, or by means of storage batteries (accumulators) which are charged either directly from the street current or by the current of a small dynamo located in the building and driven by the street current.

The highest electromotive force required for the quantitative precipitation and separation of the metals and for most other electrolytic work does not exceed 10 volts, while the pressures of the currents received from the street are ordinarily 110, 115, 220, 230, and even 500 volts. The economical transformation of these to currents of the low voltages which are adapted to laboratory purposes is a matter of much importance.

The too common practice of charging small storage batteries by inserting resistance in the line from the street until the current normal for the particular type of cell is obtained is attended by an enormous loss of energy.

The voltage of the charging current should only slightly exceed the counter electromotive force of the battery. All excess of the former over the latter is wasted. Suppose, by way of illustration, that a battery consisting of four cells with a normal charging rate of 12.5 amperes is to be charged. Arranged in series, the battery toward the close of the charging period will have an electromotive force of 10 volts, 2.5 volts per cell. The maximum work to be done is, therefore, $10 \times 12.5 = 125$ watts, or 0.168 horse power. Suppose, however, that the battery is charged from a line on which the pressure is 115 volts, resistance being inserted until a current of 12.5 amperes is obtained, the work accomplished in charging the battery or lost in heating

the resistance will be $115 \times 12.5 = 1437.5$ watts, or 1.927 horse power. In other words, the waste of energy amounts to more than 91 per cent. As the number of cells in series increases, the waste diminishes. But to charge economically with a current of 115 volts, the number of cells which must be placed in series is, approximately, $\frac{11.5}{2.5} = 46$. Similarly, if the pressure upon the charging line is 230 volts, the number of cells should be nearly 92, etc. Such large-batteries are, however, not ordinarily necessary, and even when currents equal to their capacities are needed, it is more economical, and less troublesome, to employ suitable dynamos unless great steadiness of current pressure is required.

If a dynamo is to be used and there is no opportunity to utilize power employed for other purposes in the building, a

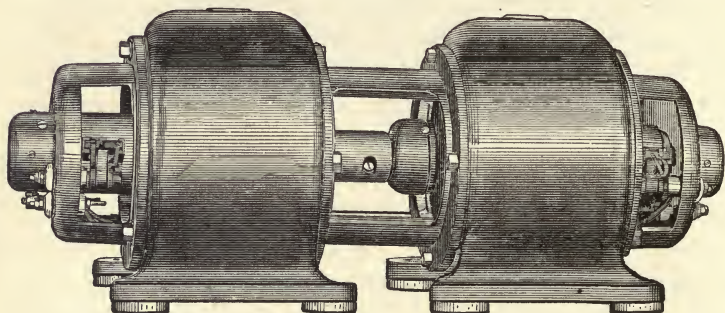


FIG. 67

motor to run it must be provided. A motordynamo, or rotary transformer like the Crocker-Wheeler machine shown in Fig. 67, is in every way satisfactory. These machines are built in a great variety of sizes from one-sixth horse power upwards. In some of them the motor and dynamo armatures are separately wound upon a single shaft, each having its own field. Either end may operate as a motor or as a dynamo, or if, as in some cases where power is available, the shaft is extended and provided with a pulley, the machines may be employed as double dynamos to furnish currents of different pressures. The armature of the

motor is wound to suit the voltage of the street current, while that of the dynamo is wound to meet the needs of the laboratory. The dynamo is provided with a field rheostat by which the voltage of its current may be economically cut down step by step to any required extent. The size of the machine will, of course, depend upon the amount of work to be done, while the character of the dynamo winding will be determined by the nature of that work. If the motor is one horse power, the output of the dynamo will probably be somewhat over 600 watts, and the latter may be wound so as to secure any desired relation of pressure to current, provided, of course, the product of the two does not exceed the maximum rated output. For example, if the output of a dynamo is 600 watts, it may be wound so as to give a current of 60 volts and 10 amperes, 10 volts and 60 amperes, 6 volts and 100 amperes, 20 volts and 30 amperes, or 30 volts and 20 amperes, etc. The maximum current (but not more) may be generated at any of the lower voltages which are secured by throwing resistance into the field.

A storage battery of moderate size is always convenient, even where dynamos are employed, and in preparing specifications for a machine, its use as a battery charger should be kept in mind and provided for. We will suppose that for the ordinary work of the laboratory a current of 25 amperes and 10 volts is required, but that a battery of eight elements with normal charging rate of 25 amperes is to be maintained, and it is desired to charge them all simultaneously, i.e. in series, which would call for a current pressure of 20 volts. In this case a dynamo with an output of 500 watts and wound to 20 volts and 25 amperes would answer both purposes. Used as a charger, the maximum voltage of the dynamo would be utilized, while at other times it would be cut down to one-half — with little waste of energy — by throwing resistance into the field.

An automatic cut-out should be inserted in the line from the dynamo to the battery to break the circuit and thus prevent a return of the battery current through the armature whenever

the dynamo, from any cause, fails to generate. All circuits, moreover, should be provided with safety fuses.

Another form of machine which may be used with advantage wherever the work to be done is continuous and varies but little in quantity is the so-called dynamotor, Fig. 68. Dynamotors differ from motordynamos in that the motor and dynamo armatures are wound together upon the same core, so that a single field suffices for both motor and dynamo. The voltage of the current generated by these machines is constant and cannot be economically regulated, as in motordynamos, by changing the resistance in the field. They are much used as battery chargers,

electroplaters, telephone ringers, and in telegraphy.

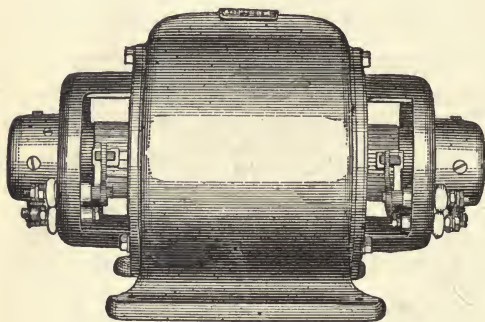


FIG. 68

For work through considerable resistances, e.g. 50, 100, or 200 ohms, dynamos of relatively large electromotive force and moderate current should be used. An example will illus-

trate the advantage of such a machine over one with small electromotive force and large current when the resistance to be overcome is high. Suppose the resistance of a circuit is 100 ohms. A dynamo with an output of 500 watts, if wound for 20 volts and 25 amperes, would send a current of $\frac{20}{100} = 0.2$ ampere through the circuit; while another machine with the same output and consuming the same amount of energy in its motor, if wound for 100 volts and 5 amperes, would give $\frac{100}{100} = 1.0$ ampere, i.e. five times as much current. There is also a great waste of energy in using dynamos of high electromotive force when the resistance to be overcome is small, for then additional resistance must be inserted in the circuit to prevent the machine from

generating more than its normal maximum of current. It is well, therefore, to have two motordynamos in a laboratory, one of low electromotive force and large current for work involving small resistance, such as the precipitation and separation of metals, and another of comparatively large electromotive force for work in which higher resistance is to be dealt with.

It is frequently necessary to take a current of low electromotive force from one of high pressure. This may be accomplished by inserting in the circuit a lamp, or two or more lamps in parallel, and a rheostat, and regulating the rheostat until the required current is obtained. Or a rheostat may be inserted in the line and a portion of its resistance short-circuited by means of a shunt. The voltage of the shunted current will equal the fall in potential between the two points where the shunt joins the main line. It should be remembered, however, that the cutting down of pressure by these methods is attended by a great waste of energy.

The currents obtained from dynamos are usually somewhat unsteady owing to fluctuations in the speed of the machines. Hence, when currents of great constancy are required, storage batteries, rather than dynamos, should be employed.

STORAGE BATTERIES

The storage battery (accumulator, secondary or reversible battery) is a device for the conversion of electrical into chemical energy which may be reconverted into electrical energy when needed. It consists essentially of two series of parallel and rigidly connected lead plates immersed in sulphuric acid of 1.2 specific gravity. The plates of one series, taken together, constitute the positive electrode, while those of the other series constitute the negative electrode. They are so spaced and arranged in the liquid that every positive plate lies between two negative ones, there being usually one more of the latter than of the former. The alternating negative and positive

plates are kept from accidental contact and therefore from short circuits within the cell by inserting between them at intervals narrow strips of hard rubber or of some other nonconducting material. Owing to the large surface of the plates, the internal resistance of the battery is exceedingly small.

If the two series of plates are covered with lead sulphate and suspended in dilute sulphuric acid, and a current from an external source is passed through the cell, the lead of the sulphate is converted on the plates belonging to the pole by which the current enters into peroxide, while on the plate belonging to the pole by which the current leaves the cell it is deposited as a spongy metal. The two series of plates thus acquire different and characteristic colors, — the first a dark brown and the second a light slate color. The brown or oxide-covered plates, together with the heavy lead bar to which they are joined, make up the positive electrode, while the negative electrode consists of the slate-colored plates. The so-called “active” material, which before charging is lead sulphate and after charging is lead peroxide on the positive and metallic lead on the negative electrode, is originally deposited upon and within the plates by various patented processes.

If the two poles of a charged cell are connected, the spongy lead on the negative plates is converted into sulphate, and simultaneously an equivalent amount of peroxide on the positive plates is reduced by hydrogen to the lower oxide, which is then converted also into sulphate. Meanwhile a current passes from the negative to the positive plates within, and from the latter back to the former without the cell. The following tentative explanation has been given for the conduct of the battery during the discharging and charging periods. When charged, i.e. when the negative plates are properly supplied with spongy lead and the positive plates with peroxide, the liquid contains sulphuric acid and lead sulphate in the electrolytically dissociated condition. In the vicinity of the positive plates there is probably also some dissociated peroxide, that is,

quadrivalent lead ions together with an equivalent number of hydroxyl ions. Suppose now the poles are joined and that an atom of spongy lead at the negative pole is dissolved, i.e. passes into the liquid carrying its two charges of positive electricity. The consequences would be twofold. In the first place, the pole would be negatively charged; secondly, two hydrogen ions belonging to the dissociated sulphuric acid would be compelled to leave the solution. This they may do by uniting at the positive pole with two hydroxyl ions belonging to the dissociated peroxide. The lead ion would thus be reduced from the quadrivalent to the bivalent condition, giving up simultaneously two of its four positive charges of electricity to the adjacent pole. In this way the two poles would become oppositely charged to the same degree. The bivalent lead would, of course, react with sulphuric acid, forming sulphate and water.

Suppose, when the battery is in the discharged condition, i.e. when the plates of both poles are covered with lead sulphate and the liquid is saturated with the same compound, that a current from an external source is passed into it at the positive pole, and that a lead ion carrying two charges of electricity receives two more and separates from the solution with four hydroxyl ions derived from dissociated water. The liquid would now contain too many hydrogen ions by two, and this would compel the deposition of a molecule of hydrogen or an equivalent amount of lead upon the negative pole. As a matter of fact, the lead is deposited.

The acid which is used in a storage battery should be free from metals other than lead, from arsenic, and from hydrochloric and nitric acids. Its concentration should be maintained by adding distilled water from time to time to replace the water which is lost by evaporation. When set up for the first time, the cells are in the discharged condition; that is, most of the lead which takes part in the chemical reactions is in the form of sulphate. The charging should begin immediately after placing the electrodes in the acid and should be continued at

“normal rate” with the least possible interruption until it is finished. It takes much longer to charge a battery for the first time than for any subsequent recharging. For example, a battery whose normal rate is 12.5 amperes for 8 hours will require the same current for nearly 30 hours when it is first set up. Though the first charge should be at normal rate, that is, at the maximum rate suitable for the particular type of cell, the battery may be recharged with smaller currents. The time required, however, will be proportionately increased. If a battery may be charged in 8 hours with a current of 12.5 amperes, it will require $8 \times 12.5 = 100$ hours to charge it with one ampere.

When charged for the first time, it is recommended by the manufacturers to discharge the battery about one-half and then to recharge it immediately, and to repeat this treatment two or three times, or until the color of the positive plates is a deep brown and that of the negative plates a light slate. The voltage of the charging current should only slightly exceed the counter electromotive force of the battery.

There are certain facts connected with the charging of a battery which require attention in order that it may be known whether the process is advancing normally and when it is to be discontinued:

1. In discharging, the voltage of a cell is not allowed to fall below 1.8. On recharging, the electromotive force of the cell rises quickly to perhaps 2.35 volts, where it remains during the larger portion of the charging period. Later it rises quite rapidly to 2.5 volts. At this point the charging should be discontinued. If cells which have been discharged to different degrees are in series, some of them will be filled before others. In this case the charging current should not be allowed to flow through the whole series until all the cells are full. Each cell should be cut out as soon as its electromotive force reaches 2.5 volts. This may be done, but the voltage of the charging current should be correspondingly diminished, or a resistance equal to that of the cells retired should be inserted in the circuit.

2. When the charging of a cell is nearly finished, i.e. when most of the lead of the sulphate produced in discharging has been reconverted into peroxide at the positive pole or deposited as metal at the other electrode, it begins to "gas" because of the liberation of oxygen at the positive and of hydrogen at the negative pole; and finally the evolution of gas becomes so rapid as to give the liquid the appearance of boiling. At this stage the cell should have an electromotive force of 2.5 volts, and the negative plates should exhibit the characteristic slate color. If a cell fails to "gas" after a reasonable period, it should be examined for a short circuit, which may occur in consequence of a warping of the plates or of the presence of conducting material between them. In prying the plates apart or dislodging material which has fallen between them, a rod of hard rubber or of wood — and never a metallic one — should be used.

3. During the discharge of a battery much of the sulphuric acid is converted into lead sulphate, which, owing to its sparing solubility, is mostly deposited upon the plates. The consequence of this disappearance of acid from the solution is a lowering of the specific gravity of the liquid, which is lightest, of course, when the battery is fully discharged. On recharging, the acid is regenerated and the specific gravity of the liquid increases, reaching its maximum when there is no more sulphate to be decomposed. Hence, if care is taken to maintain a nearly constant volume of liquid in a cell by replacing the water lost by evaporation, one can judge quite accurately of its condition by simply taking the specific gravity of the liquid.

4. As noted already, the electromotive force of a cell should not be allowed to fall below 1.8 volts. When this point is reached, it should be recharged with the least possible delay. If the discharge has been carried too far, or if a cell has been allowed to stand in the discharged condition, it should be recharged at half rate and until the potential rises to 2.4 volts.

The charged cell has an electromotive force of 2.5 volts only while the charging current is flowing. On discontinuing the

current, the potential falls to 2.2 volts, and soon after beginning to discharge it sinks to about 2 volts. From this point the loss of electromotive force is gradual.

If a battery is to be "put out of commission" for a time, the manufacturers recommend the following procedure: It is first fully charged. The acid is then removed by means of a siphon, and the jars are immediately filled with water. Lastly, the battery is discharged until the potential sinks below one volt per cell, when the water is withdrawn. To bring the battery into use again, it is to be treated as if it were receiving its first charge.

ELECTROLYSIS

1. THE ELECTRODES

A simple platinum dish with a capacity of 200 or 250 cc. serves well as a cathode for the deposition of most metals. In order that a good contact between the dish and the negative wire of the circuit may be secured, a heavy brass plate is provided with a binding screw at one end and is hollowed out in the middle to fit the bottom of the dish. If the contents of the dish are to be warmed during an electrolysis, as they frequently must be, a piece of asbestos board is laid upon a tripod or upon the ring of an iron stand, and upon this are placed the brass plate and the dish. A small flame under the asbestos easily raises the temperature of the liquid in the dish to 50° or 80° without danger that the boiling point will be reached.

A suitable anode, or positive electrode, is made from a disk of heavy platinum foil 50 mm. in diameter. To the center of this is attached a stout platinum wire about 150 mm. in length. To secure a good contact between the wire and the disk the former is flattened at one end and bent to a right angle. The disk is laid on a hard, smooth, and nonconducting surface,—e.g. on a porcelain block,—the flattened portion of the wire is placed upon the center of the disk, and the parts in contact are heated

with the flame of the blast lamp. When quite hot the parts can be firmly welded by striking with a small hammer. The disk should be provided with a considerable number of small holes for the escape of gas, which otherwise would accumulate under it and interfere with the electrolysis. These should be made by inverting the disk on a block of wood and punching it with an awl. If the holes are made from the upper side of the disk, gas will collect and remain under the electrode, owing to the downward direction of the conical elevations produced by the awl.

The dish is to be covered during an electrolysis with a watch glass which has been bored in the center to accommodate the standard of the anode. Such holes are easily made in glass by boring with a piece of tempered steel, using a solution of camphor in turpentine as a lubricant. An efficient boring implement for the purpose may be made by grinding to proper shape, and then tempering, the soft end of a small file. The point of the drill should be quite fine and must have a number of sharp edges.

A great variety of other forms have been proposed for electrodes and some of these are in general use for particular determinations, such as that of copper, but the platinum dish and disk described above are satisfactory for nearly every kind of electrolytic deposition.

A convenient stand for electrodes is shown in Fig. 69. The standard on which are mounted the brass ring with its three platinum points for the support of the platinum dish and the clamp for the anode, consists of a stout glass rod.

The relation of the area of an electrode used as cathode to the quantity of the current determines, to a great extent, the character of the metallic deposits. If the current is large and the electrode small, the rapid separation of metal upon the limited surface is apt to give poorly adhering and even spongy deposits;

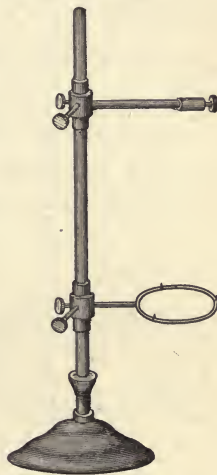


FIG. 69

while if the current is small and the electrode large, the deposits lack uniformity of thickness and present the appearance of irregular patches. It is therefore necessary to select a unit of electrode surface and to define the *density* of the current with respect to it. The unit chosen is 100 square centimeters, which is designated by the symbol ND_{100} . If the current is 1 ampere and the area of the electrode is 100 square centimeters, the density is said to be 1 ampere with respect to the electrode; while if the electrode were half as large, — 50 square centimeters in area, — the density would be 2 amperes, etc. In precipitating metals, the density of the current with respect to the cathode is of importance, but the anode may be of any convenient size.

2. RHEOSTATS

The current is regulated to the requirements of the work in hand by means of rheostats. The form of the instrument shown in Fig. 70 is to be recommended. These rheostats are made

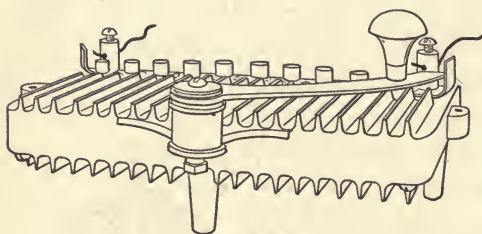


FIG. 70

with any range of resistance and to carry with safety any quantity of current which the purchaser may designate. Three small instruments, with ten steps each, when connected in series, will

give every degree of resistance from 0.1 ohm to 111 ohms, by tenths of a unit, if the resistances of the three are respectively 10 ohms, 1 ohm, and 0.1 ohm on each step. In other words, with such an arrangement, 1110 different combinations can be made. It is well to construct the rheostat of highest resistance with more than 10 steps, since each additional step in this instrument makes possible a hundred new combinations. There is no subdivision or multiplication of the resistance that is likely

to be desired which cannot be effected by the system. For instance, if a fourth rheostat with 0.01 ohm resistance on each step is added to the series, the number of possible combinations rises immediately to 11,110. It should be borne in mind in preparing specifications for rheostats that the higher the required resistance the finer must be the wire, and that fine wires cannot carry large currents. In other words, it is impracticable, as it is also unnecessary, to combine large current-carrying capacity with high resistance. In general, only rheostats of small resistance are required to carry large currents.

3. FARADAY'S LAWS

1. When a current is passed through an electrolyte, the quantities of the ions which separate at the poles are proportional to the intensity of the current. For example, if 1 ampere in 1 second (1 coulomb) precipitates 0.0011172 gram of silver, then 2 amperes will precipitate 2×0.0011172 gram in the same time.

2. If a given current is passed through any number of electrolytes arranged in series, the weights of the ions which separate at the various poles are related to each other as their chemically equivalent weights. If, for instance, a current passes through three cells in series, the first containing a solution of a silver salt, the second a salt of zinc, and the third a cupric salt, the weights of the metals precipitated upon the three cathodes will be related as $107.11 : \frac{64.9}{2} : \frac{63.1}{2}$.

The weights of the ions which are chemically equivalent are found, of course, by dividing their atomic weights—or the sum of the weights of the atoms contained in them if they are complex—by their respective valencies.

The so-called electro-chemical equivalent of an ion is the weight of it which is separated at an electrode by 1 coulomb of current,—that is, by 1 ampere in 1 second. It may be readily found in any case (if the system of atomic weights based on the

weight of hydrogen as unity is employed) by multiplying the atomic weight of the ion or the sum of the weights of the atoms in it, by 0.0000104304 (the electro-chemical equivalent of hydrogen) and dividing by the valence of the ion.

It is to be noted that metals which, like copper, mercury, iron, etc., form more than one series of salts with electro-negative elements or groups, have also more than one electro-chemical equivalent. The equivalent of copper, for example, is 0.0003292 gram in cupric salts, and 0.0006584 gram in cuprous salts. In ferric salts the equivalent of iron is 0.00019331 gram, and in ferrous salts 0.00028998 gram.

To separate the number of grams of any ion which is equal to its chemically equivalent weight — e.g. 1 gram of hydrogen, 35.18 grams of chlorine, 107.11 grams of silver, 47.675 grams SO_4 , etc. — 95,874 coulombs are required.

To find what weight of any ion will be separated in a given time by a given current, it is necessary only to reduce the current and time to coulombs and to multiply by the electro-chemical equivalent of the ion.

To find what current will be required to separate a given weight of any ion in a fixed time, the weight is divided by the electro-chemical equivalent of the ion, and the quotient by the time in seconds. The second quotient will be the number of amperes which must be employed.

A necessary conclusion from the facts embraced by Faraday's law is that ions of equal valence carry equal charges of electricity, positive or negative; also that bivalent ions carry twice as much as univalent ions, etc., — in other words, that the magnitude of the charge carried by an ion is strictly proportional to its valence.

The current enters a solution at the anode or positive electrode, and leaves it at the cathode or negative electrode. The ions which move toward the anode are negatively charged and are called *anions*, while those which move toward the cathode, i.e. in the direction of the current, are positively charged and are called *cations*.

4. POLARIZATION CURRENTS

The metal which is deposited upon the cathode during the progress of an electrolytic separation tends to return to the ionic condition owing to its so-called electrolytic solution pressure. The same phenomenon presents itself whenever any separation takes place upon insoluble electrodes, whether the deposits are solids or gases. The result is an electromotive force or "polarization current" in the cell opposed to that which is producing the deposition. In order, therefore, that a metal may be precipitated or, more generally, that any kind of electrolytic separation may be effected, a current must be employed whose electromotive force is superior to that of the polarization current. Otherwise no continuous separation will take place. These statements do not apply to cells like plating baths, in which the anodes are made of the plating metal and are therefore dissolved as fast as the metal is deposited on the cathode. In such cells there is no polarization current in the usual sense.

Le Blanc has determined the magnitudes of the electromotive force which just suffices for the decomposition of a number of substances in normal solutions. The following values were found for salts from which the metal is precipitated:

ZnSO_4	= 2.35 volts	$\text{Cd}(\text{NO}_3)_2$	= 1.98 volts
ZnBr_2	= 1.80 "	CdSO_4	= 2.03 "
NiSO_4	= 2.09 "	CdCl_2	= 1.88 "
NiCl_2	= 1.85 "	CoSO_4	= 1.92 "
$\text{Pb}(\text{NO}_3)_2$	= 1.52 "	CoCl_2	= 1.78 "
AgNO_3	= 0.70 volt		

The decomposition values of the common acids and bases were:

Acids

Hydrochloric	= 1.31 volts	Hydrobromic	= 0.94 volt
Nitric	= 1.69 "	Hydriodic	= 0.52 "
Sulphuric	= 1.67 "	Oxalic	= 0.95 "
Phosphoric	= 1.70 "		

Bases

Sodium hydroxide = 1.69 volts

Potassium hydroxide = 1.67 "

Ammonium hydroxide = 1.74 "

The fact that each metal requires for its precipitation a certain minimum electromotive force, below which it cannot separate from solutions of its salts, and that these minima are different for different metals, is of great practical importance, since it makes possible a satisfactory electrolytic separation of several of the metals. If, for example, a solution contains copper and zinc as sulphates, the former may be completely precipitated by a current whose voltage is kept above 1.22, but is not allowed to rise above 1.4, while all of the zinc remains in solution. On raising the voltage to 2.35 or higher, the zinc also is precipitated.

The pressure of current which is required for the electrolytic decomposition of a substance may be calculated from the heat of its formation. For example, the heat of formation of an electro-chemical gram-equivalent weight of zinc sulphate $\left(\frac{64.91 + 95.35}{2} = 80.13 \text{ grams}\right)$ is approximately 53,045 calories, while the equivalent of the calorie in electrical energy is 4.2 joules. The heat of formation of 80.13 grams of zinc sulphate is, therefore, expressed in electrical units, equivalent to 53045×4.2 , or 222789 joules; and $\frac{222789}{95874}$, or 2.32 volts, is the current pressure which must be maintained in order to effect the electrolysis of the salt. The value found experimentally by Le Blanc was 2.35 volts.

EXERCISE LVIII

ELECTROLYTIC DETERMINATIONS

1. COPPER

a. Classen's Method

Dissolve a weighed quantity (0.2 to 0.5 gram) of pure copper sulphate in a little water and add an excess of a saturated solution of ammonium oxalate. Heat to about 80° and electrolyze for a few minutes; then add from a burette with a fine outlet, at the rate of about 10 drops per minute, a saturated solution of oxalic acid, allowing the acid to fall upon the covering glass, from which it will find its way into the dish through the hole in the center of the glass.

To determine when the precipitation of the copper is finished, a drop of the liquid is taken out from time to time after about two hours, and tested on a porcelain surface with a drop of a solution of potassium ferrocyanide which has been acidified with hydrochloric acid.

At the end of the electrolysis the liquid in the dish is to be removed and replaced by water without interrupting the current. For this purpose two siphons are employed, one for the removal of the liquid and the other for the introduction of water.

Finally, the deposited metal is washed repeatedly with water and then with small quantities of alcohol, and dried in an air bath at 80° to 90° .

The conditions of the experiment as given by the author of the method are:

Temperature of the liquid, 80° .

Density of the current, $ND_{100} = 0.5$ to 1.0 ampere; most favorable density, 1.0 ampere.

Electrode tension, 2.5 to 3.2 volts.

Time, 2 hours.

The particular advantage claimed for the method is the short time required for the deposition of the metal.

In the case of quite dilute solutions of copper salts the oxalic acid may be introduced from the beginning of the electrolysis, whereas in concentrated ones such a course would result in the precipitation of a difficultly soluble oxalate of copper.

b. Deposition in the Presence of Nitric Acid

Dissolve a weighed quantity of copper sulphate in water, add 2 or 3 cc. of dilute nitric acid, and electrolyze.

Conditions of the experiment:

Temperature, 20° to 30°.

Density of the current, $ND_{100} = 0.5$ to 1 ampere, — the last only when no other metal than copper is present.

Electrode tension, 2.2 to 2.5 volts.

Time, 5 to 6 hours.

Chlorides must be absent, owing to the tendency of copper in their presence to precipitate in spongy form.

Copper can be separated from iron, nickel, cobalt, manganese, zinc, and cadmium in the manner described under *b*, but the quantity of the nitric acid must then be increased to 20 cc. (sp. gr. 1.21). It cannot be separated from antimony, arsenic, mercury, silver, tin, and bismuth.

2. NICKEL

Classen's Method

Dissolve a weighed quantity of ammonium nickel sulphate in about 25 cc. of water, warm, add from 6 to 8 grams of ammonium oxalate, and dilute the solution to 100 or 120 cc. During the electrolysis maintain a temperature of 60° to 70°. The completion of the deposition is tested with ammonium sulphide.

Conditions of the experiment:

Temperature, 60° to 70°.

Density of current, $ND_{100} = 1$ ampere.

Electrode tension, 3.1 to 3.8 volts.

Time, 3 to 5 hours.

Cobalt may be satisfactorily determined under precisely the same conditions.

Nickel and cobalt may also be determined under the conditions recommended by Fresenius and Bergmann as follows: The solution of the salt is treated with from 4.5 to 6 grams of ammonium sulphate and 40 cc. of ammonia of 0.96 specific gravity, and diluted to 150 or 170 cc. If more than 0.5 gram of the metal is to be precipitated, the quantity of the ammonia is increased to 50 or 60 cc.

Conditions of the experiment:

Temperature, that of the room.

Density of the current, $ND_{100} = 0.5$ to 0.7 ampere.

Electrode tension, 2.8 to 3.3 volts.

Chlorides, nitrates, fixed organic acids, and magnesium compounds should not be present.

3. IRON

Classen's Method

Dissolve from 6 to 8 grams of ammonium oxalate in the least possible quantity of warm water, add slowly and with constant stirring the solution of the iron salt $((NH_4)_2 FeSO_4)$. Dilute to 100 or 150 cc. and electrolyze.

Conditions of the experiment:

Temperature, 20° to 40°.

Density of the current, $ND_{100} = 1$ to 1.5 amperes.

Electrode tension, 3.6 to 4.3 volts.

Time, 3 to 4 hours.

At the close of the precipitation the dish is quickly emptied. The deposit is washed repeatedly with water and with small quantities of pure alcohol, and then dried at a temperature of 70° to 90° .

The best compounds from which to precipitate iron in the manner described above are the double ammonium sulphates. If the solutions to be electrolyzed contain chlorides or nitrates, they should be evaporated with sulphuric acid until all hydrochloric and nitric acids have been expelled. The excess of the sulphuric acid is afterwards neutralized with ammonia.

4. ZINC

Classen's Method

Owing to the difficulty of removing electrolytically deposited zinc from platinum, the dish used as cathode should first be plated on the inside with copper or silver. The former metal may be deposited in the manner described under 1, *a*, or 1, *b*. If the dish is to be plated with silver, the metal is best precipitated from a solution of its double salt with potassium cyanide by a current of 0.2 to 0.5 ampere.

Having prepared the dish, dissolve the zinc salt in the smallest possible quantity of warm water, and add about 4 grams of ammonium oxalate. Heat, adding small quantities of water if necessary until all of the salt is dissolved, and transfer the solution to the dish. Electrolyze at 50° to 60° from 3 to 5 minutes, and then introduce a saturated solution of oxalic acid or a 6 per cent solution of tartaric acid, as directed under 1, *a*.

Potassium ferrocyanide is employed to determine when the precipitation is finished. The dish must be washed without interruption of the current.

Conditions of the experiment:

Temperature, 50° to 60° .

Current density, $ND_{100} = 0.5$ to 1.0 ampere.

Electrode tension, 3.5 to 4.8 volts.

Time, 2 hours.

NOTE. — The few examples given above will serve as an introduction to analysis by electrolysis. For further information regarding electrolytic determinations and separations, the student is recommended to consult Classen's *Quantitative Analyse durch Electrolyse*, or the English translation of the same by Herrick.

CHAPTER XXII

BUTTER

The fats and oils, whether of animal or of vegetable origin, are principally made up of mixtures of the neutral glycerin salts of certain organic acids. Of these acids it may be said, in general, that they are all mono-basic and contain, in most instances, an even number of carbon atoms; also that they belong, with few exceptions, to the series represented by the formulas $C_nH_{2n}O_2$, $C_nH_{2n-2}O_2$, $C_nH_{2n-4}O_2$, and $C_nH_{2n-6}O_2$. The following table gives the composition of the more important acids, together with some examples of the fats in which their occurrence is characteristic.

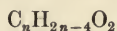
ACETIC ACID SERIES

Acetic, $C_2H_4O_2$	Rare.
Butyric, $C_4H_8O_2$	In butter, of which about 6 per cent consists of buty- rin, the neutral glycerin salt.
Isovaleric, $C_5H_{10}O_2$	In porpoise and dolphin oils.
Caproic, $C_6H_{12}O_2$	In butter and cocoanut oil.
Caprylic, $C_8H_{16}O_2$	In butter, human fat, and cocoanut oil.
Capric, $C_{10}H_{20}O_2$	In butter and cocoanut oil.
Lauric, $C_{12}H_{24}O_2$	In laurel oil, cocoanut oil, spermaceti, etc.
Myristic, $C_{14}H_{28}O_2$	In nutmeg butter, Dika oil, and cocoanut oil.
Palmitic, $C_{16}H_{32}O_2$	In most animal and vegetable fats and oils.
Stearic, $C_{18}H_{36}O_2$	In most fats.
Arachidic, $C_{20}H_{40}O_2$	In arachis oil.
Behenic, $C_{22}H_{44}O_2$	In oil of behen.

ACRYLIC ACID SERIES

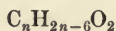
	$C_nH_{2n-2}O_2$
Tiglic, $C_5H_8O_2$	In croton oil.
Oleic, $C_{18}H_{34}O_2$	In most fats and oils.
Erucic, $C_{22}H_{42}O_2$	In rape oil.

LINOLIC ACID SERIES



Linolic, $C_{18}H_{32}O_2$ In linseed and other drying oils.

LINOLENIC ACID SERIES



Linolenic, $C_{18}H_{30}O_2$ In linseed and other drying oils.

The chemical methods which are employed to distinguish genuine butter from the various manufactured substances resembling it (oleomargarine, butterine, etc.), and to determine whether butter has been adulterated with other fats or oils, are all based on a single characteristic difference in composition between butter, on the one hand, and all those fats, on the other, which can be successfully employed to counterfeit or adulterate it. This difference lies in the fact that butter contains a considerable proportion of the glycerin salts of acids of comparatively small molecular weight, — butyric, caproic, caprylic, and capric, — while the other fats, with possibly one exception, are nearly destitute of them.

These acids of low molecular weight are soluble in water and can therefore be readily separated from those of high molecular weight, like palmitic, stearic, and oleic acids, which are insoluble in water. On this difference is based the process of Hehner, to whom belongs the credit of having been the first to propose a rational method for distinguishing butter from its admixtures with other fats, and from oleomargarine.

They are also volatile with water vapor, while the other acids occurring in fats and oils are either nonvolatile, or only slightly volatile with steam. This is the basis of Reichert's method.

Again, since butter contains a larger proportion of acids of small molecular weight, it follows that a fixed weight of it requires more alkali for its saponification than the same weight of other fats. On this fact is founded the method of Koettstorfer.

EXERCISE LIX

DETERMINATION OF THE INSOLUBLE ACIDS

HEHNER'S METHOD

Melt about 100 grams of butter in a beaker glass, taking care not to raise the temperature unnecessarily, and filter the upper oily portion through a dry, warm paper into a large test tube. Place the tube in water having a temperature of 50° or 60° , and keep it there until the oil appears to be free from water. Filter through a dry, warm paper into large weighing glasses, taking care not to allow any water which may have separated from the butter to come upon the filter. Stir the filtrate while it is solidifying in order to prevent any separation of the constituents.

Place a filter, of double thick paper and about 100 mm. wide, in a weighing glass and dry it to constant weight at 100° .

Weigh about 2 grams of the butter into a beaker glass and add to it 50 cc. of 85 per cent alcohol and a piece of pure potassium hydroxide weighing from 1 to 2 grams. Heat the beaker gently upon a water bath from 20 to 30 minutes. Add water, drop by drop, stirring the liquid after each addition. If it remains clear, the saponification is complete. If it becomes turbid, the addition of water must be stopped and the heating continued. Evaporate the alcohol and dissolve the residue in about 150 cc. of water. Add to the clear solution a moderate excess of dilute hydrochloric acid. Heat until the insoluble acids collect in liquid form at the top and the solution beneath becomes quite clear. Place the weighed filter in a funnel, fitting it tightly to the glass. Pour boiling water through it, and, while it is still half full of water, begin to filter the contents of the beaker. Cleanse the beaker thoroughly with the boiling water, and wash the acids on the filter with not less than $1\frac{1}{2}$ liters of boiling water. Place the filter, while it is still somewhat damp, in the weighing glass in which it was previously dried, and heat to very nearly constant weight at 100° .

The insoluble acids, according to Hehner, the author of this method, constitute from 86.5 to 87.5 per cent of genuine butter, though in some cases the percentage rises to 88. In other fats and oils the percentage of insoluble acids is, as a rule, about 95.5. He would therefore regard as spurious any specimen of reputed butter which is found to contain more than 88 per cent of these acids. To calculate the extent of the adulteration, where a higher per cent has been found, he assumes that 87.5 is the normal percentage of insoluble acids in butter, and finds the proportion of the foreign fats by means of the difference between that number and the higher per cent which the sample contains. Accordingly, a specimen which yields 91 per cent of insoluble acids would be regarded as containing 43.75 per cent of foreign fats, since $95.5 - 87.5 = 8$, and $91.0 - 87.5 = 3.5$, and $8 : 3.5 :: 100 : 43.75$.

The conclusions of Hehner regarding the quantity of insoluble acids which is normal to butter have been repeatedly verified, but not by all observers. Some have found 89 and even over 90 per cent of insoluble acids in butter whose genuineness could not be questioned.

The following table gives the percentage of insoluble acids which several of the fats and oils have been found to contain.

Butter	87.50	Olive oil	95.43
Lard	96.15	Palm oil	95.60
Tallow	95.50	Peanut oil	95.00
Oleomargarine	95.56	Rape oil	95.10
Cocoanut oil	86.43	Sesame oil	95.48
Cotton-seed oil . . .	95.75		

A portion of the soluble acids of the butter is lost during saponification in consequence of the formation of volatile ethyl salts.

If the liquid under the layer of insoluble acids is turbid at the time of filtration, the filtrate will also be cloudy from the presence in it of insoluble acids in a finely divided condition. It is therefore important to postpone the filtration until the liquid becomes quite clear. A slight turbidity can be removed

by passing the filtrate repeatedly through the filter. The filtrate should be carefully examined, not only with respect to its clearness, but also for the presence in it of minute globules of the insoluble acids.

The washing of the insoluble acids is the most critical feature of the determination. In the liquid condition they dissolve considerable quantities of the soluble acids and retain them with great tenacity. The water should be forced into the funnel in such a way as to break up the layer of insoluble acids to the greatest possible extent. In this manner a much larger surface is brought into contact with the water, and the removal of the soluble acids is correspondingly more rapid. The water in the funnel should be allowed to drain out quite completely before introducing a fresh portion. A very faintly alkaline solution of phenolphthalein may be used to test the reaction of the filtrate.

The insoluble acids cannot be dried to a perfectly constant weight in the air. According to Hehner they lose for a time and then gain in weight in consequence of oxidation. However, a fairly satisfactory approach to constancy may be obtained if the soluble acids have been completely removed by the washing process.

The weight of the insoluble acids may be obtained by placing the filter, after drying it in a current of air, in a Soxhlet apparatus and extracting it with ether. The ether is then distilled off and the residue heated to constant weight at 100°.

EXERCISE LX

DETERMINATION OF THE VOLATILE ACIDS

REICHERT'S METHOD

Weigh very nearly 5 grams of the butter, prepared as directed under LIX, into a quarter-liter Erlenmeyer flask. Add to it 10 cc. of 95 per cent alcohol which has been treated with a

little sodium hydroxide and then redistilled, and 2 cc. of a caustic soda solution made by dissolving 100 grams of sodium hydroxide in 100 cc. of water. Attach the flask to an inverted condenser and heat for one hour in a water bath, immersing the flask nearly to the neck in the boiling water. Evaporate the alcohol and dissolve the residue in 135 cc. of recently boiled water. To the clear soap solution, when its temperature has fallen to 60° or 70°, add 5 cc. of dilute sulphuric acid, prepared by diluting 200 cc. of the strongest acid to one liter. Attach the flask to the inverted condenser and heat until the insoluble acids collect in a clear oily layer at the top. Allow the contents of the flask to cool to the temperature of the room. Introduce a few pieces of pumice stone which have been thrown into water while at a white heat and kept there until needed. Attach the flask to a condenser arranged for distillation and distill off 110 cc. in 30 minutes as nearly as possible. Receive the distillate in a narrow graduated cylinder so that the rate of the distillation may be properly regulated. Filter the distillate, after shaking it well, through a dry paper. Titrate 100 cc. of the filtrate with a tenth-normal solution, either of barium hydroxide in water or of potassium hydroxide in alcohol, using an alcoholic solution of phenolphthalein as the indicator. Add one-tenth for the portion of acid not titrated.

According to Reichert and many other chemists who have tested his method with care, the distillate from 2.5 grams of genuine butter neutralizes from 13 to 15 cc. of tenth-normal alkali; while that from an equal weight of any other fat or oil which could be successfully employed to adulterate or imitate butter neutralizes, generally, less than 2 cc. Possibly an exception should be made in the case of cocoanut oil, whose distillate has been found to neutralize from 3.5 to 3.7 cc. of tenth-normal alkali. Reichert would regard as certainly adulterated, or as consisting of other fats than butter, any sample whose volatile acids neutralize less than 12.5 cc. of alkali. The following table gives, in cubic centimeters, the quantity of tenth-normal

alkali required to neutralize the volatile acids derived from 2.5 grams of some of the fats and oils.

Butter	13.0 to 15.0	Cocoanut oil	3.70
Lard	0.30	Palm-nut oil	2.40
Tallow	0.25	Palm oil	0.80
Oleomargarine	0.95	Rape oil	0.25
Cotton-seed oil	0.30	Sesame oil	2.20

Only about four-fifths of the volatile acids in the butter are found in the distillate, and the quantity which a distillate of given volume will contain varies somewhat with the volume of the liquid distilled and the rapidity of the distillation. Hence the necessity of following fixed rules as to the volume of the liquid distilled, the volume of the distillate collected for examination, and the time within which the distillation is made.

It is preferred by some to effect the saponification in a strong flask, which is closed during the reaction by a cork securely tied to the neck.

EXERCISE LXI

DETERMINATION OF THE ALKALI REQUIRED FOR SAPONIFICATION

KOETTSTORFER'S METHOD

Dissolve about 10 grams of potassium hydroxide in 2 liters of 95 per cent alcohol and redistill. Dissolve about 15 grams of the purest potassium hydroxide in 400 or 500 cc. of the redistilled alcohol and dilute with the same to one liter. Pour the solution into a bottle and allow it to stand undisturbed until the potassium carbonate which was in the hydroxide settles out and becomes firmly attached to the glass.

Prepare a standard solution of hydrochloric acid, each cubic centimeter of which contains the quantity of acid required to neutralize 11.14 milligrams of potassium hydroxide. Weigh

from 1 to 2 grams of butter into a small Erlenmeyer flask and add to it the volume of the alcoholic potash solution which has been found to be equivalent to 40 cc. of the standard acid. Attach the flask to an inverted condenser and heat it on a water bath until the saponification is complete. Allow the flask to cool to the temperature of the room before removing it from the condenser. Add an alcoholic solution of phenolphthalein and titrate the excess of alkali with the standard acid.

Koettstorfer found that one-gram quantities of genuine butter from different sources required for saponification from 221.5 to 232.4 milligrams of potassium hydroxide, while an equal weight of various other fats and oils required a much smaller amount of the alkali. The following table gives in milligrams the quantity of potassium hydroxide required to saponify one gram of the substances named.

Butter . . .	221.5 to 232.4	Olive oil . . .	189.3 to 192.6
Lard . . .	192.0 to 196.5	Palm oil . . .	196.3 to 202.5
Tallow . . .	193.2 to 198.0	Palm-nut oil . .	220.0 to 247.6
Butterine . .	193.5 to 196.5	Peanut oil . . .	196.6
Cocoanut oil .	246.2 to 268.4	Rape oil . . .	170.2 to 176.4
Cotton-seed oil	191.0 to 196.6	Sesame oil . . .	190.0 to 192.4

Experiments made in this laboratory indicate that the quantity of alkali required to saponify one gram of butter obtained from milk by evaporating the water and extracting the residue with ether is quite exactly 230 milligrams.

It was found by Moore that one gram of a mixture consisting of 49.3 per cent of cocoanut oil and 50.7 per cent of oleomargarine required for its saponification 220 milligrams of potassium hydroxide. An equal quantity of another mixture of the same substances containing 70.2 per cent of cocoanut oil and 29.8 per cent of oleomargarine required 234.9 milligrams.

EXERCISE LXII

DETERMINATION OF THE ALKALI NEUTRALIZED BY THE SOLUBLE AND THE INSOLUBLE ACIDS

METHOD OF MORSE AND BURTON

There are required for this determination a solution of potassium hydroxide in alcohol and one of hydrochloric acid. It is not necessary to know the strength of either solution. They should, however, be quite dilute and approximately equivalent. The solutions used in the preceding exercise will answer very well for this. It is also unnecessary to weigh the butter.

Place a quantity of butter, judged to weigh not more than two grams, in a small Erlenmeyer flask and add to it a measured but excessive quantity of the alkali. Attach the flask to an inverted condenser and heat it on a water bath until the saponification is complete. Allow the flask to cool to the temperature of the room and then titrate the excess of the alkali with the solution of hydrochloric acid, using phenolphthalein as the indicator. Attach the flask to a condenser arranged for distillation. Immerse it to the neck in water and distill off all the alcohol, collecting the distillate for subsequent use. Draw off a number of cubic centimeters of the alkali equal to the number which was added to the butter in the first place and titrate with the acid. Having found how much acid is required to neutralize the whole of the alkali, and also the alkali which remained after saponification, add an amount of the acid equal to the difference between these quantities to the soap in the flask. It is also well to add from 50 to 75 cc. of water. The quantity of acid added is, of course, just sufficient to liberate all the acids of the butter. Attach the flask to the inverted condenser and heat it on a water bath until the insoluble acids have collected in an oily layer at the top and the liquid below has become quite clear. The minute globules of molten insoluble acids sometimes remain suspended for a long time, giving

the liquid a milky appearance. If filtration is attempted while the liquid is in this condition, some of the finely divided insoluble acids will pass through the filter. The difficulty can be remedied in either of two ways: first, by introducing a small quantity of long-fiber asbestos and rotating the flask for a few minutes; or, second, the liquid may be allowed to cool and stand for a few hours. In the latter case the suspended acid solidifies and rises to the top, and on reheating, the liquid below the oily layer is usually found to be free from suspended globules. Filter through a double-thick paper which has been saturated with water, and wash the insoluble acids as directed under LIX. Add the alcoholic distillate to the filtrate and titrate with the alkali. Dissolve the insoluble acids in hot alcohol and titrate them with some of the same alkali.

Express the relation of the quantities of the alkali necessary to neutralize the soluble and the insoluble acids in the form of percentages of the whole amount of the alkali which was required to saponify the butter.

It is evident that the sum of the volumes of the alkali used in neutralizing the two classes of acids must equal the volume of the alkali required for the saponification. This fact furnishes a check of some value upon the correctness of the work.

The following table gives the percentages of alkali required to neutralize the soluble and the insoluble acids in butter, coconut oil, cotton-seed oil, oleomargarine, lard, and tallow.

	Per cent KOH required for Insoluble Acids	Per cent KOH required for Soluble Acids
Butter	86.57	13.17
Cocoanut oil (unwashed)	91.95	8.17
Cocoanut oil (washed with hot water) . .	92.43	7.42
Cocoanut oil (washed with dilute Na_2CO_3) .	92.33	7.45
Cotton-seed oil	92.05	7.76
Oleomargarine	95.40	4.57
Lard	95.96	3.82
Beef tallow	96.72	3.40

It was found by Moore that a mixture of 50, per cent of butter, 27.5 per cent of oleomargarine, and 22.5 per cent of cocoanut oil could not be distinguished from genuine butter, either by the method of Hehner or by that of Koettstorfer. Such a mixture, examined by this method, gave 90.17 per cent KOH required for insoluble acids; 9.70 per cent KOH required for soluble acids.

EXERCISE LXIII

DETERMINATION OF THE IODINE ABSORBED

HÜBL'S METHOD

Dissolve iodine, 12.5 grams, and mercuric chloride, 15 grams, each in 250 cc. of 95 per cent alcohol. Filter the mercuric chloride solution, if necessary. Mix the two solutions and allow the mixture to stand for twelve hours.

Dissolve about 24 grams of sodium thiosulphate in water and dilute to a liter. Determine the strength of the solution in the usual manner with resublimed iodine.

Test the chloroform which is to be used by adding to 10 cc. of it 10 cc. of the iodine solution. After three hours determine the iodine in the chloroform and also in 10 cc. of the original iodine solution. The quantities of iodine found should be the same.

Dissolve 25 grams of potassium iodide in 250 cc. of water.

Prepare a one per cent starch solution in the usual manner.

Weigh about 0.8 gram of butter into a 200-cc. Erlenmeyer flask. Dissolve it in chloroform. Add 20 cc. of the iodine solution. Close the flask with a rubber stopper and shake it. If the solution becomes cloudy, add a little more chloroform. Close the flask and allow it to stand 2 hours. If the color of the solution fades to any considerable extent, add more of the iodine solution. The excess of the iodine must be quite large. Add from 10 to 15 cc. of the potassium iodide solution and shake well. Dilute with 150 cc. of water. Titrate with the thiosulphate solution until the color becomes quite faint, then add starch paste and

titrate to the end-reaction. Draw off a quantity of the iodine solution equal to that added to the butter in the first place. Add potassium iodide and determine the iodine in it. The difference between the quantities of iodine found by the two titrations is equal to the quantity which has been absorbed by the butter.

The quantity of the iodine absorbed is stated in the form of percentage, by weight, of the butter taken. The number of parts of iodine absorbed by one hundred parts of any fat or oil is known as its "iodine number." The following table gives the iodine number of several of the fats and oils.

	HÜBL	MOORE	ARCHBUTT
Almond oil	97.5-98.9	98.1	—
Olive oil	81.6-84.5	83.0	—
Rape oil	97.0-105.0	101.0-104.0	—
Sesame oil	105.0-108.0	102.7	—
Cotton-seed oil	105.0-108.0	106.0-109.0	—
Linseed oil (raw)	156.0-160.0	155.2	—
Linseed oil (boiled)	148.0	—	—
Castor oil	84.0-84.7	—	84.3
Menhaden oil	—	—	147.9
Sperm oil	—	—	84.3
Neat's-foot oil	66.0	—	71.9
Palm oil	50.4-52.4	50.3	—
Cocoanut oil	8.9	8.9	—
Cocoa butter	34.0	—	—
Japan wax	4.2	—	—
Butter	26.0-35.1	19.5-38.0	—
Oleomargarine	55.3	50.0	—
Lard	59.0	61.9	—
Tallow	40.0	—	—

It will be observed that the iodine number of butter, as given in the table, varies between wide limits. The lower values, however, were obtained from samples which were in an advanced stage of decomposition.

It has been shown by Moore that the addition of cocoanut oil in certain proportions to lard, to oleomargarine, and to a mixture of

butter and oleomargarine, gives products whose iodine numbers are about equal to that of genuine butter. It was also found by him, as previously stated, that certain mixtures of cocoanut oil with other fats yield the same results as butter when tested by the methods of *Hehner* and *Koettstorfer*. All such mixtures are, however, readily distinguished from butter by the method of *Reichert*.

It is doubtful whether cocoanut oil — which, if it were added in the right proportions, would render the methods of *Hehner*, *Koettstorfer*, and *Hübl* useless in butter analysis — is, or can be, successfully employed in adulterating butter or in the manufacture of its substitutes. Its taste and odor seem to render such a use of it impracticable.

The chief value of *Hübl*'s method lies in its efficiency as a means of detecting the adulterations of oils.

EXERCISE LXIV

DETERMINATION OF BUTTER IN MILK

I. DETERMINATION BY THE ORDINARY GRAVIMETRIC METHOD

To about one liter of commercial ether, in a strong bottle, add thin shavings of metallic sodium. Close the bottle with a cork having a groove on one side, or with one through which a glass tube with a small outlet has been passed. When the sodium becomes so much incrustated as to prevent contact between the ether and the metal, clean it by pressing and rubbing the pieces against the bottom of the bottle with a stout glass rod. Continue to clean the metal from time to time, adding more of it, if necessary, until the evolution of hydrogen ceases. Keep the ether in the bottle with an excess of sodium until it is needed for the extraction of the butter.

Ignite some asbestos in a platinum dish over a blast lamp and place a portion of it in a "*Hofmeister*" capsule, — a thin glass shell which can be readily crushed.

Measure 10 cc. of well-shaken milk into a large weighing glass. Close the glass and weigh it. Pour the milk upon the asbestos in the capsule. Close the glass and weigh it again.

Evaporate to dryness in a steam bath consisting of a liter-Erlenmeyer flask, and a funnel having a diameter of about 120 mm. at the top and a wide neck. Pass the neck of the funnel through a cork which fits the flask, and provide a rest for the capsule by placing a small triangle in the bottom of the funnel, or by hanging glass rods with curved ends over the edge of it.

FIG. 71^aFIG. 71^b

Prepare a filter for the Soxlet apparatus, Figs. 71^a and 71^b, which is to be used in the extraction. For this purpose a cylinder of wood or other material is required. It must be square and smooth at one end, and of somewhat smaller diameter than the extraction apparatus. Wind a strip of the best and strongest filter paper twice around the cylinder, allowing one edge to extend considerably beyond the square end, and fasten it with pins. Fold in the free edge upon the end of the cylinder and press the folds against some hard object. If necessary, the folds may be secured in their places by wiring them together. If it is feared that the bottom of the filter will permit solid material to pass through it, a little paper pulp suspended in water may be poured into the filter and the water drawn off with the pump as in the preparation of a Gooch filter. The filter should be long enough to extend from the bottom of the extractor to the point where the ether vapors enter it, and so wide that no place will be left between the paper and the glass.

Filters especially made for the Soxlet apparatus can now be obtained and are to be preferred to the one described above.

Distill on the water bath a quantity of the ether which will somewhat more than fill the extractor. Place the dry filter and a roll of filter paper in the extractor and extract them with the redistilled ether for 2 hours. The heat should be so regulated during the extraction that the apparatus will fill and siphon off in four or five minute periods. Great care must be exercised in selecting the corks by which the different parts of the apparatus — the inverted condenser, the extractor, and the flask — are joined together. The flask should be heated in an air bath and not in water. A thin iron crucible somewhat larger than the flask answers very well as a bath. The heat rising from the bath sometimes interferes with the automatic action of the siphon. This difficulty is easily remedied by placing a shield of cardboard between the bath and the extractor.

Place the capsule containing the dried milk, bottom upwards, in a porcelain mortar. Cover the mortar with a piece of cardboard having a hole in the center just large enough for the pestle. Hold it in place with the fingers of one hand, and, with the pestle in the other hand, crush and grind the capsule and its contents. Transfer the ground material to the filter, and place it in the extractor. Pour a little ether into the mortar and rub it over the inside with the pestle. Then pour the ether down a glass rod into the filter. Continue washing the mortar in the same manner with small quantities of ether until it is believed that all the fat has been removed from it. Cover the contents of the filter with some of the extracted paper. Attach a weighed flask containing ether to the extractor, and extract the filter for not less than 4 hours. Distill off the ether and dry the butter residue to a constant weight at a temperature of 60° or 70°. During the latter part of this process a current of dried air should be drawn through the flask to facilitate the removal of the last traces of the ether.

Having found the weight of the butter, determine, by the method of Koettstorfer, how much potassium hydroxide is required to saponify it.

The ether, when not in use, should be returned to the main supply in the bottle containing metallic sodium.

II. DETERMINATION BY ADAMS' METHOD

Cut off strips of thick filter paper, 65 mm. wide and 600 mm. long. Roll them up loosely and extract thoroughly with anhydrous ether. Measure 5 cc. of well-shaken milk into a weighing glass and weigh. Open one of the rolls and stretch the strip of paper — horizontally and at some distance above the table — between two clamps. Distribute the milk as uniformly as possible over the central portion of the paper. Close the glass from which the milk was taken and weigh it. Place a heated air bath under the paper, and when it appears to be nearly dry, roll it up loosely. Place the roll on a watch glass in the air bath and heat for an hour at 100°. Put the roll into the filter in the extractor and extract with anhydrous ether for not less than 3 hours. Proceed with the extract as directed under I.

Instead of opening the roll of extracted paper and distributing the milk in the manner described above, the roll may be tied with a thread and one end of it dipped into the milk. When the milk has all been absorbed, the roll is placed on the unsoiled end in a watch glass and dried at 100°.

Having found the weight of the butter, determine how much alkali is required to saponify it.

III. DETERMINATION BY THE METHOD OF MORSE, PIGGOT, AND BURTON

In this method the milk is dried by means of anhydrous copper sulphate and the fat extracted either with the low-boiling products of petroleum or with ether. In the former case the quantity of the butter is to be determined by saponification.

Prepare a quantity of anhydrous copper sulphate by heating the recrystallized salt in a porcelain dish at a temperature of

250°. It may be prepared more expeditiously by heating the salt upon a copper plate with the naked flame; but, in that case, the material must be constantly stirred and not allowed to harden upon the metal.

In a porcelain mortar—provided with a lip and having a diameter of 90 or 100 mm. at the top—place about 20 grams of the anhydrous copper sulphate. Make a depression in the center with the pestle, and pour into this a weighed 10-cc. portion of milk. Draw the copper sulphate which was pushed aside in making the cavity into and over the milk, and, while the mass is still somewhat moist, begin to grind with the pestle. Continue the grinding until the material is reduced to a fine powder, and extract it with ether in the Soxhlet apparatus.

CHAPTER XXIII

ELECTRIC HEATING APPLIANCES FOR LABORATORY USE

The advantages of employing electricity for heating purposes in the laboratory are numerous.

1. The heat required can be generated within the space to be heated, — that is, where it is needed.

2. Since the heat is generated where needed, it can be economized very effectively by surrounding the heated space with nonconducting materials and confined air spaces.

3. With practically constant electromotive force, such as we have in the storage battery, the temperatures can be controlled with a high degree of exactitude.

4. Having once calibrated an electric heating device, — that is, having determined for each temperature the resistance of the portion of the circuit in which the heat is generated, — one can thereafter at any time ascertain the temperature without the aid of thermometer or pyrometer.

5. Where calibrated electric furnaces or baths are used, it is feasible in many cases to ascertain at what temperatures reactions take place and to determine when they begin and cease.

6. There is no contact of the substances heated, with deleterious products of combustion, as often happens when gas is used.

7. Heating by electricity is much less destructive than heating by gas to the materials used in the construction of furnaces, baths, etc.

8. Owing to the less destructive effects upon costly materials and to the practicability of preventing waste through loss of heat to the outside air, and of so adjusting the resistance of the heating device to the electromotive force of the current that

little is lost in external resistance, heating by electricity is, in many operations, more economical than heating by gas.

Some of the appliances in use in the author's laboratory in which the electric current is utilized for heating purposes are here described.

1. CRUCIBLE FURNACE

Figure 72 represents a furnace for heating materials, — fusion of silicates, etc., in platinum crucibles. The three hard-burned perforated clay rings, *a*, *b*, and *c*, are held in place by three

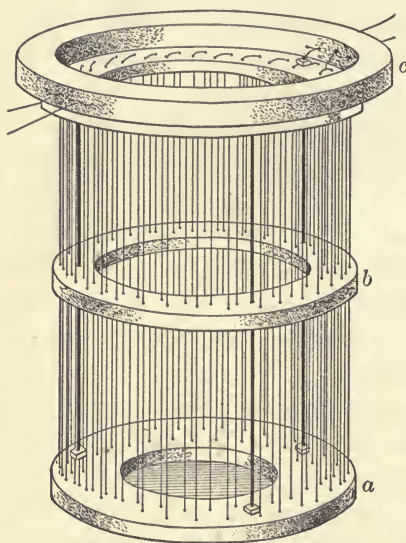


FIG. 72

platinum rods made from No. 16 wire (B. & S. gauge). The ends of these rods are threaded and each end is provided with two small platinum nuts between which the rings *a* and *c* are firmly fastened. The purpose of the ring *b* is to keep the crucible from coming in contact with the platinum wires. It is adjustable up or down, but may be fixed in any desired position by twisting short pieces of wire about the rods. The internal diameters of *b* and *c* are equal, while that of *a* is smaller in order to fur-

nish a rest for the crucible support. Each ring is provided with 60 perforations in two rows of 30 each, through which the platinum wire (No. 26 B. & S. gauge) is threaded up and down in the manner shown in the figure. The inner row of wires also crosses from side to side under *a*. The total height of the furnace, as represented in the figure, is 80 mm., and the total length of the wire is 16 feet. The platinum rods serve

two important purposes. They support the whole weight of the furnace and its contents, and thus prevent any stretching of the wires while hot; and, having at all times about the same temperature as the wires, they keep the latter perfectly straight, and thus prevent any danger of short circuits through contact between adjacent strands.

The furnace as represented in Fig. 72 is surrounded by the clay cylinder *d*, as shown in Fig. 73, the ring *c*, Fig. 72, resting upon the upper edge of *d*. The cylinder *d* is provided with the perforated cover *e* and the

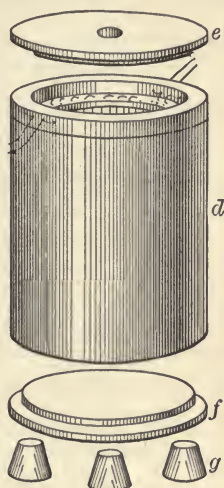


FIG. 73

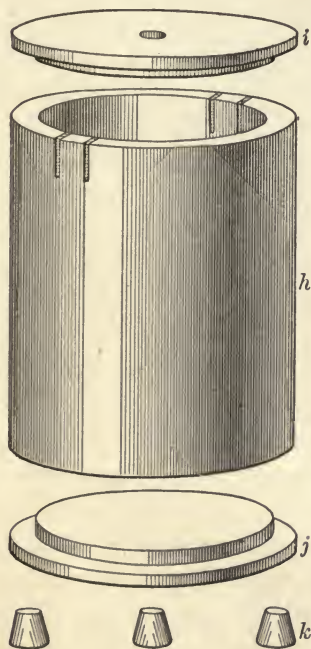


FIG. 74

bottom *f* which rests upon the three truncated clay cones *g*. The hole in *e* serves for the introduction of a thermometer or pyrometer. Figure 74 represents a cylinder *h* of larger dimensions which surrounds *d*. It is also furnished with a perforated cover *i*, a bottom *j*, and the supports *k*.

The complete furnace is shown in Fig. 75, in which *l* is a Le Chatelier pyrometer; *m*, a galvanized iron cylinder with cover, — both of which are lined and covered with asbestos paper; *n*, a series of asbestos boards with ventilating spaces between them; *o*, a block of soapstone; and *p*, a wooden board on which the whole

arrangement rests and can be moved without disturbing any of the parts; *q* and *r* are firmly fixed steel rods which serve to

connect the wires coming from the furnace with the external circuit and to protect the former from injury through strains of any kind; *s, s* are short pieces of pipestem which keep the platinum wires from contact with the metallic cylinder *m*. The crucible support *t* is made as light and open as possible, coming in contact with the crucible at three points only.

The method of making the clay parts and the process of wiring this furnace have been described in the *American Chemical Journal* for 1904.

The first step to be taken with a furnace of this kind is to calibrate it, — that is, to determine its resistance for every temperature up to the limit to which it is afterwards to be heated; for it will then be feasible at all times, without the aid of a thermometer or pyrometer, to maintain in it with certainty any desired temperature, or to ascertain at any time what the temperature in it is. The furnace, in fact, becomes, by virtue of such a calibration, a resistance pyrometer.

For the calibration of the furnace in use in the author's laboratory there were employed a mercury thermometer registering to 550°, a Le Chatelier platinum-platinum-rhodium pyrometer, and a Keiser-Schmidt decimillivoltmeter, all of which had been tested at the German Physikalisch-Technischen Reichsanstalt. We give below in tabular form the data for the furnace up to 967°. The calibration was not carried higher because the temperature 950° is sufficient for ordinary crucible work. The temperatures given are probably correct to within 5° or less. The voltmeter which was used to measure the electromotive force which was developed at the junction of the platinum and platinum-rhodium wires is furnished with two scales, — one in which each division has the value of a decimillivolt, and another in which a division corresponds to 20° of temperature. Notwithstanding the coarseness of the needle in this instrument, the errors of parallax in reading could not have amounted to more than one-fourth of a division on either scale.

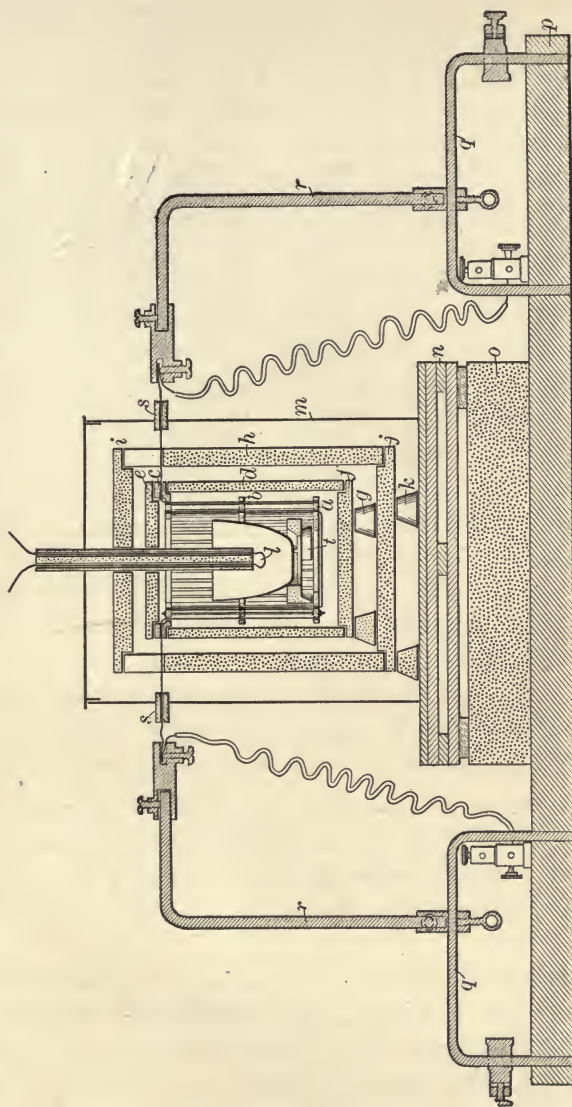


FIG. 75

CURRENT	VOLTAGE	RESISTANCE	WATTS	TEMPERATURE
2.5	33.7	13.48	84.25	383°
2.6	36.0	13.846	93.60	407
2.7	38.5	14.259	106.38	434
2.8	41.0	14.671	114.80	463
2.9	43.6	15.034	126.44	488
3.0	47.4	15.80	142.20	526
3.1	50.2	16.193	155.62	558
3.2	52.7	16.468	168.72	587
3.3	55.3	16.757	182.49	615
3.4	58.3	17.147	198.22	640
3.5	61.2	17.486	214.20	663
3.6	64.3	17.861	231.48	690
3.7	66.9	18.081	247.53	710
3.8	70.1	18.447	266.38	741
3.9	73.3	18.795	285.87	766
4.0	76.3	19.075	305.20	793
4.1	79.5	19.390	325.55	813
4.2	82.5	19.643	338.25	840
4.3	85.3	19.837	366.79	867
4.4	88.7	20.159	390.28	888
4.5	92.0	20.444	414.00	914
4.6	95.0	20.652	437.00	940
4.7	98.0	20.851	460.60	967

Unless absolutely unavoidable, a calibrated furnace like the foregoing should not be heated above 1150°. At higher temperatures the metal is volatilized to an extent which sensibly affects the resistance of the wires, making a recalibration necessary.

It will be readily understood that an accurately calibrated resistance furnace is theoretically an admirable instrument for the study of reactions at high temperatures; for, if external conditions are constant, it will always require the same amount of electrical energy to maintain any given temperature in the empty furnace, or, what is the same thing, a given amount of electrical energy is bound to maintain in it always a certain fixed

temperature. If now any reaction involving the disappearance or evolution of heat takes place within the heated space, the amount of electrical energy required to maintain the temperature at which it takes place will be increased or diminished according as the reaction is endothermic or exothermic. And the difference, if it can be ascertained, will serve as a measure of the heat energy of the reaction. There is little difficulty in discovering at what temperature reactions involving considerable heat effects take place in such an electric furnace. If, for instance, a substance is losing water in the furnace, it will be noticed that the amount of current required to maintain the temperature as determined by the resistance is considerably greater than that required to maintain the same temperature in the empty furnace, showing that a reaction involving the loss of heat is going on within. Again, when a fusible substance is heated in the furnace and the temperature of fusion is reached, there is noticed an increase in the flow of the current without any corresponding increase in the resistance of the platinum wire, i.e. in the temperature within the furnace. The increased flow of current continues for a time and then diminishes to its original volume, showing that the fusion is finished. If the furnace has been calibrated, a determination of its resistance during the time of the increased flow of current will give the melting point of the substance. In this way it was found that the fusing point of sodium carbonate is between 860° and 863° . The exact time of fusion may also be ascertained by arranging to have the sinking of a platinum weight into the softened material either close or break a circuit in which there is a sensitive ammeter.

Notwithstanding the favorable location of the wires in this furnace with respect to the space heated, and the double-inclosed air spaces surrounding it, the temperature within does not immediately rise to its maximum when the current passing through the furnace is increased, — that is, some time elapses before the temperature within adjusts itself to that of the

external atmosphere. The tardiness of this adjustment between internal and external conditions lessens somewhat the precision of the results obtained when the furnace is employed for the investigation of reactions at high temperatures. It is, however, to be hoped that a remedy will be found for this defect of a method which is otherwise so promising.

2. AIR BATHS WITH GRAPHITE STOVES

Graphite is a substance which conducts electricity, but differs from metallic conductors in that its conductivity increases with rise of temperature. If it could be evenly distributed in sufficient quantity over a smooth surface and made to adhere to the same with sufficient tenacity, it should afford a ready means of raising temperature by electricity up to that at which graphite is burned by the oxygen of the air.

Unfortunately the rubbing of ground dry graphite upon a smooth surface does not give a sufficiently heavy coating of the material to conduct the requisite amount of current. A thicker covering can be obtained by repeated applications of it, in a wet condition, with a flat camel's-hair brush. The surface to which it is applied must, however, be hot enough to evaporate the water almost instantaneously; otherwise the deposit will be quite uneven. The results obtained by the last method are nevertheless unsatisfactory. The material lacks adhesiveness, and when an attempt is made to harden it by polishing with a stiff brush, much of the graphite is detached, and the surface which is produced is easily injured by handling or by contact with other objects.

To secure a satisfactory deposit, some other material must be mixed with the graphite, and all of the substances which lend themselves to this purpose are incapable of withstanding as high temperatures as graphite itself. There are two substances with which the graphite may be mixed with excellent results so far as the conducting surface is concerned: first, washed and bolted

clay, and second, some kinds of soap. Of these the former is much to be preferred.

The best results are secured with the paste form of a well-known stove polish which is obtainable everywhere in this country, and this material is to be recommended for the preparation of graphite stoves above any mixture of graphite with clay or with soap which can be made in the laboratory.

Soapstone is undoubtedly the

best of all available materials on which to spread the graphite for heating purposes. It is easily cut to any desired form; its surface can be made very smooth, which is essential to the best results; and, above all, it withstands better than any other non-conducting material great and sudden changes of temperature.

Figures 76 and 77 represent two forms of graphite stoves for ordinary hot-air baths. *a*, Fig. 76, is a soapstone block of convenient size for

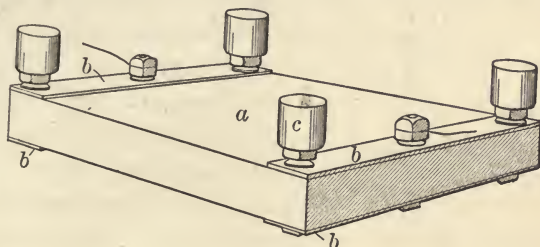


FIG. 76

the usual rectangular copper air bath. It is seen in place in Fig. 78. *b, b, b, b* are strips of iron which are bolted to the block at the

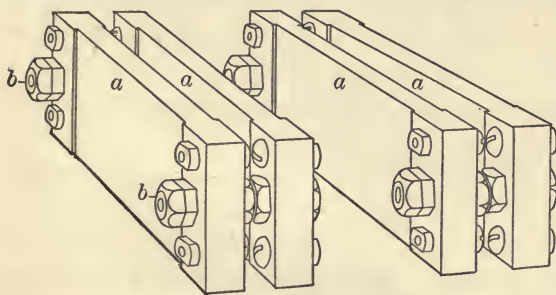


FIG. 77

ends, the central bolt at each end serving for the attachment of the wires of the circuit. The corner bolts, which are longer than the others, are covered with the soapstone caps *c, c, c, c*. On these rests the perforated metallic shelf, as seen in Fig. 78.

Figure 77 represents another arrangement for heating the same bath, which has the advantage that the surfaces on which the heat is generated are vertical. *a, a, a, a* are strips of soapstone of such dimensions that when bolted together by twos, as shown in the figure, three pairs of them can rest on the bottom of the bath, leaving room between the ends for the insertion of mica plates to prevent electrical contact. Each end of every soapstone strip is provided with two iron plates which are bolted to the stone in the manner shown. Two strips, thus furnished, are fastened together by the longer bolts *b, b*, which are also utilized

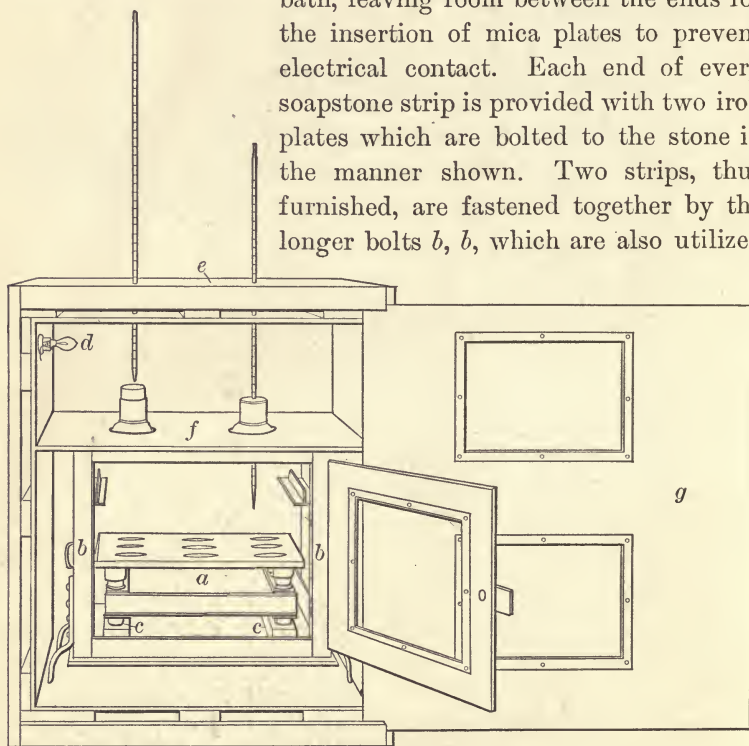


FIG. 78

for the attachment of wires. Figure 78 represents the arrangement as a whole. *b* is a copper bath of the usual form having a mica window in the door. The stove *a*, which may be of either of the forms represented in Figs. 76 and 77, rests on the soapstone strips *c, c*. The inner vertical walls of the copper bath may be lined to advantage with thin asbestos board, but in

that case it is well to cover the exposed surface of the board with aluminium paint, which will prevent the lodgment of dust and the shedding of particles of asbestos. The wires of the stove pass horizontally through the sides of the copper bath and the outer compartment to the exterior of the wooden box which incloses the whole, where each wire terminates in a binding post screwed into the box. Where the wires pass through the copper walls they are prevented from coming in contact with the metal by short pieces of clay pipestem. When a stove such as is shown in Fig. 77 is used, each of the three pairs of plates is provided with independent wires and binding posts, any required combination of the individual pairs, in parallel or in series, being made more conveniently on the outside than on the inside of the bath. *d* is a diminutive electric lamp of small voltage, which serves to illuminate the scales of the thermometers. The current for it comes through a shunt from the stove, and a switch is fastened to the outside of the box for the purpose of closing and breaking the lamp circuit. The voltage of the lamp must be suited, of course, to the fall in potential of the stove. The interior of the wooden box is lined on all sides except the front with asbestos board so as to leave confined air spaces between the asbestos and the wood. The surface of the lining boards is also covered with aluminium paint. *f* is a closely fitting shelf of asbestos board (also painted) which rests upon the copper bath and is supported at the ends. *g* is a door which slides in grooves in the wooden box. It contains two mica windows and is made from asbestos board.

The shelf *f* divides the interior of the box into two compartments whose temperatures will differ quite widely from each other and from the temperature which is kept in the copper bath. This difference can, however, be diminished, if desired, by replacing *f* by a more or less open shelf which permits circulation of air between the upper and lower spaces. Each of the heated compartments, including the copper bath, should be provided with two properly located ventilating tubes, running to

the outside of the wooden box. Porcelain insulating tubes are well adapted to this purpose. They may be closed with corks to prevent loss of heat when not needed.

The data which were obtained in testing two such baths as have been described are given below. They will serve as a basis for estimating the economical advantage of employing electricity instead of gas to heat ordinary baths.

Bath No. 1 was like that shown in Fig. 78. The stove was of the kind represented in Fig. 76. The temperature to which the bath was tested was 250°, which is as high as copper should be heated. The temperatures given in the first column are the temperatures of the copper bath, while those in the second column are the temperatures of the upper compartment. The third column gives the current; the fourth, its fall of potential within the bath; the fifth, the number of watts consumed; and the sixth, the number of hours which a kilowatt will maintain the temperatures recorded in the first and second columns.

Bath No. 1

Temperature in Copper Bath	Temperature in Upper Compartment	CURRENT	FALL IN POTENTIAL	WATTS	Hours per Kilo- watt
100°	48°	1.73 amp.	15.9 volts	27.5	36.36
125	58	2.10 "	18.8 "	39.48	25.58
150	65	2.50 "	21.4 "	53.50	18.69
175	72	2.77 "	23.2 "	64.26	15.56
200	85	3.16 "	25.5 "	80.58	12.41
225	96	3.48 "	27.0 "	93.96	10.75
250	106	4.07 "	29.2 "	118.84	8.41

Bath No. 2 differed from No. 1 only in that a stove of the kind represented in Fig. 77 was used. It was tested between 150° and 258°.

Bath No. 2

Temperature in Copper Bath	Temperature in Upper Compartment	CURRENT	FALL IN POTENTIAL	WATTS	Hours per Kilo- watt
150°	73.0°	1.20 amp.	40.3 volts	48.36	20.67
175	83.5	1.39 "	44.5 "	61.85	16.10
200	95.0	1.61 "	49.0 "	78.89	12.60
225	104.5	1.89 "	51.5 "	97.33	10.20
258	111.0	2.53 "	50.0 "	126.50	7.90

An even distribution of the conducting material over the surface of the soapstone is of great importance; for, if it is unevenly distributed, the resistance in different regions will vary and more heat may be developed at some points than at others. The result, in the case of a carelessly prepared stove, is that the graphite burns out in certain spots, while the heat developed upon the whole surface is much less than it ought to bear with safety. The process of applying the graphite, or, rather, the stove polish, is given in some detail.

The iron plates at the ends of the soapstone block (Fig. 76), or of the strips (Fig. 77), are removed and their inner surfaces, and also the portions of soapstone which are covered by the plates, are evenly spread with a rather thick layer of the paste. The plates are then replaced and bolted together. The block, or strip (connected in the circuit in which there is also an ammeter), is placed on a piece of asbestos board or of some other nonconducting material which is heated over a lamp. When the stone is hot enough to evaporate water with rapidity but without "sputtering," the paste, much thinned with water, is evenly applied with a flat camel's-hair brush whose width is about 25 mm. The whole stone should be covered each time, but the brush should not pass more than once over any one spot. After each application the surface is vigorously polished with a stiff toothbrush. As soon as the conductivity of the

graphite covering has increased to a point where the current suffices to maintain the proper temperature of the stone, it is removed from the asbestos board and the surface is carefully explored with a voltmeter with reference to the uniformity of the distribution of resistance. The subsequent applications of graphite are regulated with a view to securing equality of conductivity over the whole surface; that is, those spots which are found by the voltmeter to exhibit a higher resistance are painted more thickly than the others. With care and a little experience it becomes easy to prepare in a short time a stove on which the graphite is very evenly distributed and so firmly adherent that it will not visibly soil the fingers in handling. As the painting proceeds, the surface is apt to become so hot that the water is evaporated with explosive violence, and the surface presents a spotted appearance, owing to an uneven spreading of the material. When this occurs the circuit must be broken and the stone allowed to cool before making an application.

In heating a bath by electricity it is necessary always to insert in the circuit a rheostat for the purpose of regulating the temperature of the bath, and, since all of the heat generated in the rheostat is wasted, it is important to reduce to a minimum the amount of resistance so employed. This can be done by regulating the thickness of the graphite covering of the stove with reference to the voltage of the current which is to be used. In other words, the stove should use up, as nearly as may be, the whole energy of the current in maintaining the required temperature within the bath. For this reason it would be better to have a stove for each temperature which it is desired to keep, e.g. one for a temperature of 100° or 110° , another for 125° , still another for 150° , etc., each utilizing nearly the whole electromotive force in keeping the temperature for which it was designed. Considerable latitude in this matter is secured by using stoves like that shown in Fig. 77, where the various pairs of plates may be used in parallel or in series, according to the temperature to be maintained and the electromotive force of the

available source of current. In preparing the stove of this kind to which the data given under "Bath No. 2" relate, the application of the graphite to each strip was continued until, with a fall of potential of 50 volts, it conducted one ampere of current. The temperature of the stone at the time of finishing the strips was not, of course, always the same, so that the resistance at any given temperature varied somewhat from strip to strip, but not sufficiently to lead to difficulties.

Before using a new graphite stove in its bath for the purpose of maintaining constant temperatures it should be made to keep in the same bath for several hours a somewhat higher temperature than the highest for which it was designed. The resistance at any given lower temperature is thereafter fairly constant. In any subsequent use of the stove the current should never be allowed to exceed that which was employed in the preliminary heating.

3. TUBE FURNACE

Figure 79 shows a cross section of a furnace for heating substances inclosed in tubes (Carius tubes, etc.). *a* is a wooden box 625 mm. in length which is so lined and covered with asbestos board as to give the confined air spaces designated by *b*. *c* is a porcelain tube having the length of the box and an internal diameter of 30 mm. The space *d* around *c* is sufficient to accommodate larger tubes when required to do so. An iron tube of thin wall is slipped into *c* to aid in distributing the heat and to prevent injury to the porcelain tube when explosions occur.

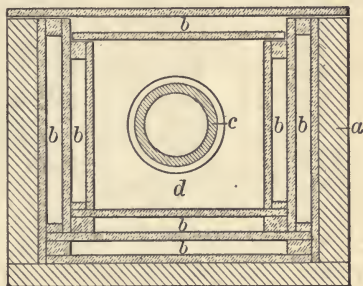


FIG. 79

Figure 80 shows an iron collar which is fastened to each end of the porcelain tube and serves for the attachment of the wires.

The graphite (stove polish) is applied to the outside of the porcelain tube in the same manner as to the soapstone surfaces, care being taken that the fall in potential shall be nearly the same for equal distances in different parts of the tube. The

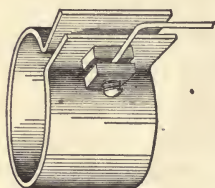


FIG. 80

paste is applied somewhat thickly under the iron rings. The following table gives the data which were obtained in testing a furnace of the kind where a covering of graphite mixed with soap instead of the usual stove-polish paste was employed. In preparing the tube a quantity of finely pulverized electrotyping graphite was made into

a thick paste by mixing it with a small quantity of a concentrated solution of hard soap. This was applied in the manner previously described.

Porcelain Tube

TEMPERATURE	CURRENT	FALL OF POTENTIAL	WATTS	HOURS PER KILOWATT
150°	1.54 amp.	28.5 volts	43.89	22.8
175	1.74 "	31.7 "	55.66	17.9
200	1.96 "	35.6 "	69.77	14.3
225	2.07 "	37.4 "	77.42	12.9
250	2.34 "	42.0 "	98.28	10.2
275	2.59 "	45.0 "	116.55	8.6
300	2.79 "	49.2 "	137.27	7.3
355	3.38 "	55.3 "	186.91	5.3

It is important for users of graphite baths to know approximately what temperature a graphite surface will bear without injury. It is unfortunate that an admixture of clay is necessary in order to improve its spreading and adhesive qualities, for the clay begins to lose its water at about 425°, and at this point a change in the resistance of the material occurs. Speaking generally, it may be stated that the temperature of the stove itself should not be allowed to rise above 400°. How nearly the

temperature of a bath may be made to approach this limit will depend, of course, upon the volume of the space to be heated as compared with the area of the heating surface. In small baths with relatively large heating surface a constant temperature of 400° may be maintained, but there is danger that in attempting to reach so high a temperature too quickly the clay will become overheated and lose some of its water. It has been found safe and practicable, with properly prepared stoves having a suitable area of heating surface, to maintain, in a considerable variety of baths, any temperature up to 350° ; and, though higher temperatures may be secured, it is at some risk to the stove. The principal danger lies in using too large a current while raising the temperature of the bath.

4. PLATINUM WIRE STOVES

For baths in which higher temperatures are to be kept than can safely be produced by graphite stoves, the arrangement shown in Fig. 81 is to be recommended. In this the resistance of a small platinum wire is utilized to generate the heat. *a* is a soapstone block, of any size to suit the dimensions of the bath, with bolts near two opposite sides, which serve to fix the coils in their places and for the attachment of the wires of the circuit. Four

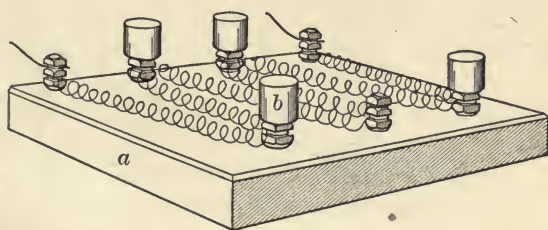


FIG. 81

of the bolt ends are covered with the soapstone caps *b*. The purpose of the caps will be made apparent by an inspection of Fig. 78. The length and size of the platinum wire are made to suit the conditions which are to be met, i.e. the size of the bath, the temperature to which it is to be heated, the voltage

of the available source of current, etc. In the furnace shown in the figure the wire is No. 32 (B. & S. gauge) and eight feet long.

To prepare the wire it is straightened, heated to redness by the current, and then wound on a threaded steel rod of the proper diameter. Such furnaces may, of course, be used in the place of the graphite stoves previously described, and the following table gives the data which were obtained while testing one of them in a bath arranged as shown in Fig. 78, except that the shelf *f* in this case was perforated so as to permit free circulation of air between the upper and lower compartments.

Bath with Platinum Wire Stove

Temperature in Copper Bath	Temperature in Upper Compartment	CURRENT	FALL OF POTENTIAL	WATTS	Hours per Kilo- watt
100°		1.08 amp.	28.5 volts	30.8	30.5
125	72°	1.24 "	34.9 "	43.3	23.1
150	80	1.4 "	41.8 "	58.5	17.1
175	89	1.6 "	51.0 "	81.6	12.3
200	110	1.77 "	59.8 "	105.9	9.5
225	125	1.89 "	66.4 "	125.5	8.0
250	144	2.00 "	73.0 "	146.0	6.9

Figure 82 represents a bath with platinum wire stove which was constructed for the purpose of heating rather large vessels to any temperature up to 500°. The heating coils of the stove *a* contained about 16 feet of No. 26 platinum wire; *b* is a terra-cotta cylinder like those used in chimneys for stovepipes; *c* is a sheet-iron cylinder which is covered inside and outside with asbestos paper; *d* and *d* are covers of asbestos board; *e* is a terra-cotta receptacle such as is used for flowerpots; *f* is sand in which the stove and the lower ends of *b* and *c* are imbedded. The dimensions of the free heated space within the bath are 250 and 175 mm. For the sake of cleanliness and of improved

appearance, *e*, *c*, *d*, and the outside of *b* are covered with aluminium paint. With temperatures within, up to 300° , it is safe to surround the outer cylinder *c* with woolen material,

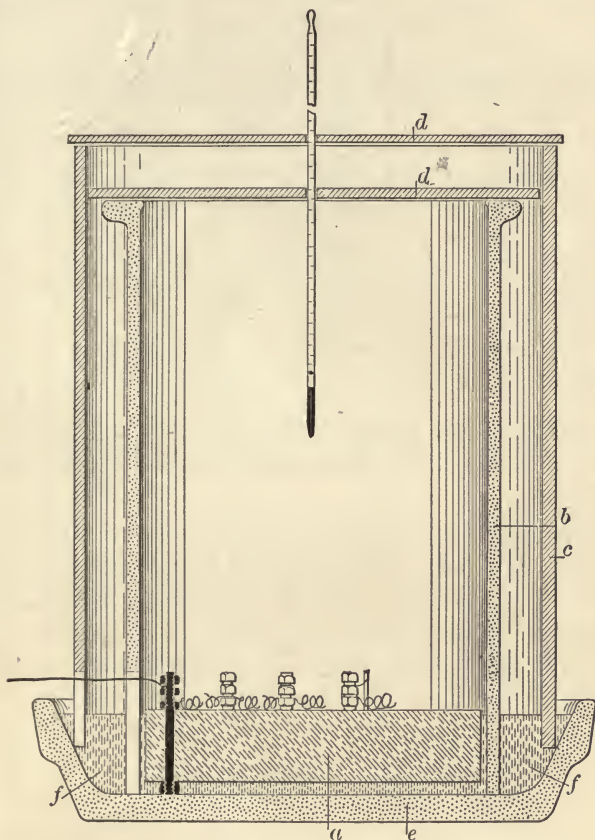


FIG. 82

or, better, with a thick pad made of hair. When higher temperatures are to be maintained, there is substituted for the pad a wooden cylinder with an internal diameter equal to the extreme width of the base *e*, and this is covered with a strip of woolen cloth. The test of this bath up to 400° , with the

thermometer bulb located in the center of the heated space, gave the following data.

TEMPERATURE	CURRENT	FALL OF POTENTIAL	WATTS	HOURS PER KILOWATT
100°	2.08 amp.	20.7 volts	43.06	23.22
125	2.20 "	23.0 "	50.60	19.76
150	2.45 "	28.0 "	68.60	14.58
175	2.70 "	32.3 "	87.21	11.47
200	2.85 "	35.7 "	100.75	9.92
225	3.04 "	40.8 "	124.03	8.06
250	3.09 "	43.0 "	132.87	7.53
275	3.29 "	48.5 "	159.57	6.27
300	3.50 "	53.5 "	177.25	5.64
350	3.73 "	61.0 "	227.53	4.40
400	4.00 "	68.0 "	272.00	3.67

The bath was not tested beyond 400° except to determine that, with a current pressure of 110 volts, its temperature rises above 500°.

Arrangements like that just described are an effective substitute for all of the oil and paraffin baths which give so much offense in the laboratory, and, like all electrically heated baths, they have the great advantage that, with a current of constant voltage, they can be regulated with a high degree of precision.

CHAPTER XXIV

AN ELECTRICAL METHOD FOR THE COMBUSTION OF ORGANIC COMPOUNDS

The process for the analysis of organic compounds which is here described is applicable to the combustion of hydrocarbons and their oxygen, halogen, nitrogen, and sulphur derivatives. The advantages which it has been found to possess over the usual method are the following: (1) The apparatus required is so compact and of such small dimensions that the analyses can be made at the working table of the student; (2) the waste of heat energy is much smaller; and (3) the time consumed in preparing for and in making a combustion is much less than by the older process.

Figure 83 represents the apparatus in its simplest form. The glass combustion tube *a* is closed at one end and has a length of 350 mm. and an internal diameter of 15 mm. Through the rubber stopper in its open end there pass (1) the porcelain tube *c* which has a length of 250 mm. and a diameter of 6 mm.; (2) the glass tube *k*, through which the products of combustion enter the absorption apparatus; and (3) a rather stout platinum wire (No. 18 B. & S. gauge), which extends from *f* to *j*. The porcelain tube *c* is joined, outside of the stopper, by means of rubber tubing, to the branched glass tube *d*. The latter is provided with a stopper through which passes the platinum wire *g* (also No. 18), which extends into the porcelain tube to the point *h*, where it is joined to a smaller platinum wire (about No. 29 B. & S. gauge). The smaller wire has a length of about $1\frac{3}{4}$ meters and weighs approximately $2\frac{1}{2}$ grams. It extends from its junction with the larger wire at *h* through the porcelain tube to the inner end of the latter, and then returns on the outside in a series of

suspended coils to the point *j*, where it joins the larger wire *f*. Thicker wire is used from *f* to *j* and from *e* to *h* in order to avoid any overheating of the rubber stopper by the current. The roll of copper wire gauze *b*, about 60 mm. in length, is inserted between the end of the porcelain tube and the boat containing the substance to be burned.

The oxygen or air which is to be used in the combustion enters the apparatus at *d*, and while passing over the portion of the small wire which is within the porcelain tube has its temperature raised more or less according to the rate of its flow. It is therefore already hot when it enters the tube *c*, where the combustion is to be effected. The excess of the oxygen and the products of the combustion of the substance pass together over the heated coils on the outside, completing the burning of any unoxidized material coming from the rear.

In the earlier work with this apparatus, stems of long clay tobacco pipes were employed; but owing to the highly porous character of this material it was found somewhat difficult to obtain satisfactory determinations of hydrogen. These stems were therefore discarded for porcelain tubes, which were made for the author at the Royal Berlin Porcelain Works. The latter have proved exceedingly durable, and they are not, of course, sensibly hygroscopic.

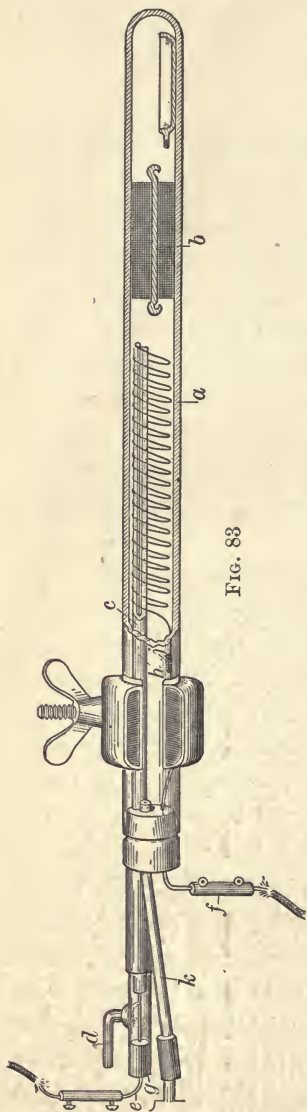


FIG. 83

The roll of copper wire gauze *b* is not absolutely necessary when the substances to be burned do not readily yield explosive mixtures with oxygen. Its presence is, however, of advantage because much less care is required in the management of the combustion with it than without it. If the substances are liquids or if they readily yield large quantities of inflammable vapors when heated, the roll of wire gauze must be inserted between the material and the end of the porcelain tube through which the oxygen enters. The objection to the use of the roll of wire gauze is that the flow of oxygen or air must be continued for some time after the completion of the combustion in order to insure the removal of all of the carbon dioxide and water from the space occupied by the boat.

The combustion is conducted in the following manner: Having placed in the positions indicated in the figure the boat containing the material and the roll of copper wire gauze (which in the beginning may or may not be oxidized), and having joined the tube *k* to the usual train of absorption apparatuses, a slow current of dry and purified oxygen is admitted and the electric current is closed through a regulating rheostat. The flow of the current is gradually increased until the wire coils assume a bright red color, when the roll of gauze *b* is heated by means of a gas lamp giving a broad thin flame to a temperature at which the copper is readily oxidized by the hot oxygen issuing from the porcelain tube. The substance in the boat is then heated with the same lamp, or with another which is held in the hand. The rate of heating and the flow of oxygen are so regulated with respect to each other that at least one-half of the roll of wire gauze is kept in the oxidized condition during the entire combustion. After the formation of volatile products has ceased, the reoxidation of the copper progresses rapidly and the oxygen enters the rear compartment, burning any residue of carbon in the boat or upon the glass. Having finished the combustion of the substance, the current of oxygen is replaced by one of dried and purified air, and the flow of the latter must, of

course, be continued until the products of combustion have all been expelled from the space behind the roll of wire gauze. It is here that a miscalculation is likely to be made. The time required for the complete removal of the products depends principally upon the freedom of diffusion through the gauze, and for this reason it should not be rolled too tightly.

The apparatus as already described is adapted to the combustion of those solids and liquids which consist of carbon and hydrogen or of carbon, hydrogen, and oxygen.

The heating of the roll of wire gauze *b*, and at times of the substance also, is facilitated by inverting over the tube, at a little distance above it, a trough made of asbestos board, the side of the trough at the back being much deeper than that in front. This arrangement is supported in its position by a rod which is inserted in a heavy block resting upon the worktable behind the tube. The device is also of advantage in protecting the tube from draughts of cold air during the combustion and during the subsequent cooling period. The portion of the glass tube which is occupied by the porcelain tube and the platinum wire is protected on the bottom by a semicircular strip of asbestos board which is inserted in the clamp between the lower jaw and the glass. To protect the upper portion of the tube in the same region, a semicircular trough of mica is inverted over it behind the clamp in such a manner that the lower edges of the mica rest in the asbestos trough below. The mica is made to keep its curved form by riveting it to narrow strips of metal and then bending the latter to the required shape.

The cooling of the tube requires some care. The current should be reduced quite gradually, and it is well also, as soon as the combustion is finished, to cover the portion of the glass tube which is beyond the porcelain one with the soot from a smoky flame, and to take any other measures for the protection of the tube which will contribute toward the proper annealing of the glass. Care must likewise be taken never to allow the platinum loops to come in contact with the glass either while

heating or cooling the tube, since in the former case the metal is likely to stick to the glass, while in the latter it is quite sure to crack at some lower temperature. If the loops are too large, the wire should be taken out and rewound.

The time required for the combustion does not ordinarily exceed half an hour, and it may be reduced to twenty or even fifteen minutes if the substance to be burned is of such a character that the roll of wire gauze can be dispensed with. Its omission is, however, not recommended except to those who have had some experience with the method. It is well to place at the end of the absorption flame a Geissler apparatus partly filled with a very dilute solution of palladium chloride in order to test the completeness of the combustion. If it is incomplete, the fact will be made apparent by the dark color developed in the solution of the palladium salt.

The consumption of electrical energy is small, amounting to about 3.7 amperes at 54 volts (194.4 watts, or about one-fourth of a horse power) during the time when the highest temperature is maintained.

At the highest temperature employed during the combustion (at a bright red, but not a white heat), especially while the wire is new, there is a sensible volatilization of platinum. This volatility of the metal in an atmosphere of oxygen, at comparatively moderate temperatures, has been repeatedly observed. In one case a platinum wire weighing in the beginning 2.3446 grams was found at the end of the thirty-eighth combustion to have lost 0.1337 gram in weight. The volatilized metal settles upon the surfaces of the glass and porcelain tubes as a dark deposit which at first may be mistaken for carbon. The presence of such films of volatilized platinum upon the inner surface of the tube is, of course, of some advantage in the combustion.

There are certain obvious objections to the use of the short closed combustion tube represented in Fig. 83. In the first place, whenever the boat is to be introduced or withdrawn, it is

necessary to remove and reinsert the rubber stopper with the tubes and wires which pass through it, and also the roll of wire

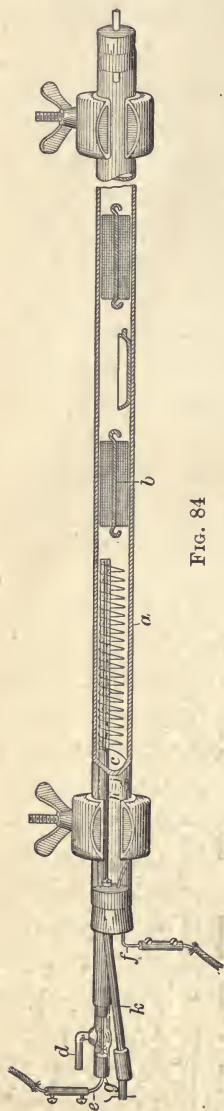


FIG. 84

gauze; and during such manipulation more or less atmospheric moisture is admitted, and the wire loops, which should remain distributed uniformly along the porcelain tube, are easily displaced and may become entangled one with another. Again, as previously mentioned, the flow of air must be continued for some time after the combustion is otherwise finished, in order to insure the complete removal of carbon dioxide and water from the space occupied by the boat. These difficulties are wholly obviated by using a somewhat longer tube which is open at both ends, as represented in Fig. 84. In this arrangement the boat is introduced from the rear, and there is placed behind it a second short roll of copper wire gauze. The stopper in the front end of the combustion tube, the forward roll of wire gauze, and also the apparatus as a whole are never disturbed. Each roll of wire gauze is heated by a lamp giving a broad thin flame, and there is inverted over both rolls and the space between them the asbestos shield already described. The lamps should be raised until the bottom of the tube is just within the blue region of the flames. In this way the overheating of the tube at certain points is effectually avoided.

To prevent any sagging of the combustion tube while hot, it is supported at a point just beneath

the end of the porcelain tube by a forked or notched standard, which is placed under the asbestos trough in which the front portion of the apparatus lies.

The combustion is conducted in much the same manner as in the short closed tube, except that in addition to the oxygen which enters the front of the tube a slow current of air or oxygen is admitted from the rear during the entire experiment. This prevents any accumulation of volatilized matter in the back part of the tube and aids in the expulsion of the products of combustion from the space occupied by the boat. If the substance to be burned is very volatile, it is advisable to introduce air and not oxygen at the rear, and to employ behind the boat a roll of gauze which is only partially oxidized. In this way the vapors of the substance may be diluted with nitrogen to any desired extent. In order to avoid any bending of the tube in consequence of its increased length while hot, the clamp at the rear is employed only as a support and is not allowed to grip the tube so tightly as to interfere with its freedom of movement back and forth.

THE COMBUSTION OF SUBSTANCES CONTAINING NITROGEN

For the determination of carbon and hydrogen in compounds containing nitrogen there is placed in the combustion tube (1) a roll, 100 mm. in length, of copper wire gauze which has been reduced in the usual way by methyl alcohol; (2) a roll 80 mm. in length, of wire gauze which has been well oxidized; (3) the boat containing the substance; and (4) a short roll of wire gauze also well oxidized.

During the combustion each of the three rolls is heated by a burner with a broad thin flame, the last lamp serving also for heating the substance, and the portion of the tube occupied by the copper is covered with a screen of asbestos board to insure a sufficiently high temperature for the reduction of nitric oxide.

The flow of oxygen through the porcelain tube is so regulated that only about one quarter of the copper roll (1) is oxidized, while at the rear it is admitted as rapidly as may be necessary to keep a portion of the second roll (2) at all times in an oxidized condition.

In the case of nitro-derivatives it is well to introduce into the boat with the substance a quantity of loose copper oxide or of finely divided silica.

The combustion of nitrogenous compounds must be conducted much more cautiously and slowly than that of other substances, owing to the necessity of burning the carbon completely before the products of the combustion reach the reduced roll of wire gauze. If the combustion of the carbon is incomplete, — that is, if a portion of it is finished in the front end of the tube, — there is danger that some of the nitric oxide will escape reduction.

THE COMBUSTION OF HALOGEN COMPOUNDS

To prepare the apparatus for the analysis of substances containing the halogens, a piece of silver foil about 50 mm. in width is rolled up in a sheet of thick paper, which is afterwards withdrawn. The silver roll is placed in the tube quite close to the end of the porcelain tube and is not directly heated during the combustion. In other respects the arrangements are the same as for the combustion of non-nitrogenous compounds. A roll of well-oxidized copper wire gauze follows the one of silver, then the boat containing the substance, and finally a second roll of oxidized copper wire gauze.

During the combustion there is formed a quantity of fusible cuprous-halogen salt, which deposits itself more or less upon the inner surface of the glass tube, but does not at any time get beyond the roll of silver foil into the space occupied by the porcelain tube and platinum wire. On cooling, the cuprous-halogen salt, in accordance with the well-known behavior of such

compounds, absorbs large quantities of oxygen, only to give it up again when the apparatus is reheated in a succeeding experiment. At the same time the copper wire in the oxidized rolls grows thinner and becomes quite brittle.

The quantity of cuprous salt accumulates after a few combustions to such an extent that the time required for its oxidation is considerable. Hence it is well frequently to cleanse the combustion tube and to renew at the same time the rolls of copper wire gauze.

THE COMBUSTION OF SULPHUR COMPOUNDS

The determination of carbon and hydrogen in compounds containing sulphur is quite simple. The only change which it is necessary to make in the arrangement for non-nitrogenous and non-halogen compounds, in order to adapt the method to the combustion of sulphur compounds, is to substitute lead chromate for the oxidized copper wire gauze which is nearest to the end of the porcelain tube. Instead of maintaining the lead chromate in its position in the tube by means of plugs of asbestos or of wire gauze, it is more convenient and better for the glass tube to introduce it in the form of a cartridge. This is prepared by filling with the loose granular chromate a shell made from fine copper wire gauze.

TABLE OF INTERNATIONAL ATOMIC WEIGHTS

	O = 16	H = 1		O = 16	H = 1
Aluminium . . . Al	27.1	26.9	Neodymium . . Nd	143.6	142.5
Antimony . . . Sb	120.2	119.3	Neon Ne	20.	19.9
Argon A	39.9	39.6	Nickel Ni	58.7	58.3
Arsenic As	75.0	74.4	Nitrogen N	14.04	13.93
Barium Ba	137.4	136.4	Osmium Os	191.	189.6
Bismuth Bi	208.5	206.9	Oxygen O	16.00	15.88
Boron B	11.	10.9	Palladium . . . Pd	106.5	105.7
Bromine Br	79.96	79.36	Phosphorus . . . P	31.0	30.77
Cadmium Cd	112.4	111.6	Platinum Pt	194.8	193.3
Cæsium Cs	132.9	131.9	Potassium . . . K	39.15	38.85
Calcium Ca	40.1	39.7	Praseodymium . Pr	140.5	139.4
Carbon C	12.00	11.91	Radium Ra	225.	223.3
Cerium Ce	140.25	139.2	Rhodium Rh	103.0	102.2
Chlorine Cl	35.45	35.18	Rubidium Rb	85.5	84.9
Chromium Cr	52.1	51.7	Ruthenium . . . Ru	101.7	100.9
Cobalt Co	59.0	58.55	Samarium Sm	153.	149.2
Columbium Cb	94.	93.3	Scandium Sc	44.1	43.8
Copper Cu	63.6	63.1	Selenium Se	79.2	78.6
Erbium Er	166.	164.8	Silicon Si	28.4	28.2
Fluorine F	19.	18.9	Silver Ag	107.93	107.11
Gadolinium Gd	156.	154.8	Sodium Na	23.05	22.88
Gallium Ga	70.	69.5	Strontium Sr	87.6	86.94
Germanium Ge	72.5	72.	Sulphur S	32.06	31.82
Glucinum Gl	9.1	9.03	Tantalum Ta	183.	181.6
Gold Au	197.2	195.7	Tellurium Te	127.6	126.6
Helium He	4.	4.	Terbium Tb	160.	158.8
Hydrogen H	1.008	1.000	Thallium Tl	204.1	202.6
Indium In	115.	114.1	Thorium Th	232.5	230.8
Iodine I	126.97	126.01	Thulium Tm	171.	169.7
Iridium Ir	193.0	191.5	Tin Sn	119.0	118.1
Iron Fe	55.9	55.5	Titanium Ti	48.1	47.7
Krypton Kr	81.8	81.2	Tungsten W	184.	182.6
Lanthanum La	138.9	137.9	Uranium U	238.5	236.7
Lead Pb	206.9	205.35	Vanadium V	51.2	50.8
Lithium Li	7.03	6.98	Xenon Xe	128.	127.
Magnesium Mg	24.36	24.18	Ytterbium Yb	173.0	171.7
Manganese Mn	55.0	54.6	Yttrium Yt	89.0	88.3
Mercury Hg	200.0	198.5	Zinc Zn	65.4	64.9
Molybdenum Mo	96.0	95.3	Zirconium Zr	90.6	89.9

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